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THE MAGNESIA SCRUBBING PROCESS AS APPLIED TO AN OIL-
FIRED POWER PLANT

George Koehler, et al

Chemical Construction Corporation

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AS APPLIED TO
AN OIL-FIRED POWER PLANT

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ABSTRACT

A full size demonstration of the magnesia wet-scrubbing system for Flue Gas Desulfurization was conducted on an oil fired, 150 MW generating unit. The project involved, first, design and construction of an SO₂ removal system based on firing 2.5% sulfur fuel and an MgO regeneration facility for 50 ton/day acid production, and then operation of both plants over a two year period. Four thousand hours of operation were logged at the generating station and the ability of the system to remove 90% of the inlet SO₂ and control particulate emissions was shown. Regenerated magnesia was recycled successfully and over 5,000 tons of acid were marketed from the regeneration plant demonstrating the feasibility of the process. Correlations were developed to determine SO₂ removal for varying boiler loads and fuel sulfur content, and to control regeneration of acceptable alkali. Several other studies of the process technology and process chemistry were undertaken as part of the work.

INDEX

	<u>Page</u>
1.0 Summary	1
1.1 Boston Edison SO ₂ Recovery System	3
1.2 Essex Chemical - MgO Regeneration and Sulfuric Acid Production	9
1.3 MgO Losses	11
1.3.1 Boston Edison	11
1.3.2 Essex Chemical	11
1.4 General	12
2.0 Background & Introduction	13
3.0 General Process Description	19
3.1 Description of Plants	24
3.1.1 Power Plant	24
3.1.2 Acid Plant	28
3.2 Description of Installed Facilities	30
3.2.1. Magnesia SO ₂ Absorption System	31
3.2.2 Magnesia Regeneration System	36
3.2.3 Acid Plant Modifications	42
4.0 Description of Work Performed	48
4.1 SO ₂ Absorption Facility Operations	48
4.1.1 End of Construction Phase	48
4.1.2 Pre-Start Up Period	50
4.1.3 Start-Up & Break-In Period	53
4.1.4 Planned Operational Tests	58
4.1.5 Operational Testing	64
4.2 Regeneration-Recovery Operations	66
4.2.1 End of Construction Phase	66
4.2.2 Pre-Start Up Period	67
4.2.3 Start-Up & Shake-Down Period	68
4.2.4 Planned Operations Tests	71
4.2.5 Operational Testing	76
4.3 Summary of System Modifications	77
4.4 System Availability	82
5.0 Equipment Arrangement & Material of Construction	87
5.1 Absorber System Areas Subject to Corrosive Attack	96

INDEX

	<u>Page</u>
5.2 Centrifuge System	107
5.3 Stack	111
5.4 Regeneration System	111
5.5 Corrosion Samples	114
6.0 Process Chemistry	119
6.1 Effect of MgO Properties on Process	120
6.1.1 Pulverization	121
6.1.2 Hydration of MgO	122
6.2 System pH & SO ₂ Absorption	122
6.2.1 SO ₂ Absorption	127
6.3 Centrifugation & Solids Separation	132
6.4 Regeneration Mechanisms	132
6.4.1 Magnesium Sulfate Control	139
6.4.2 Magnesia Activity Control	141
6.5 MgO Losses & Regeneration Cycles	141
7.0 Description of Test & Development Program	146
7.1 Test Program	147
7.1.1 Start Up & Break In Tests	147
7.1.2 Variables Screening Tests	147
7.1.3 Long Term Tests	148
7.2 Statistical Methods	148
8.0 Performance Test Results	154
9.0 Data	159
9.1 Operating Information	160
9.2 Range of Significant Variables	169
9.3 Miscellaneous Data	197
10.0 Financial Data	202
10.1 Systems Cost	204
10.2 Operating Costs	206
10.3 Process Economics	206
11.0 References	216
12.0 List of Publications	217
13.0 Conversion From English to Metric Units	219

INDEX

	<u>Page</u>
Appendix A - Magnesium Sulfite Hydrates - Transition & Formation	220
Appendix B - Physico - Chemical Data	227
Appendix C - Analytical Techniques	236

FIGURES

1	SO ₂ Removal Efficiency-Effect of ΔP	4
2	Effect of pH on SO ₂ Outlet Concentration	5
3	Calciner - Effect of Mid Kiln Temperature on Bulk Density	10
4	Fossil Fuel Steam Generating Unit Life Curve	15
5	Chemico-Basic Magnesia F.G.D. System - Schematic Flow Diagram	20
6	Sectional View of Absorber	21
7	Mystic #6 Boiler Cross Section	26
8	Damper Location & Ducts F.G.D. System	27
9	Process Flow Diagram-Absorber & Centrifuge Systems	32
10	Process Flow Diagram Drying System	38
11	Process Flow Diagram Calcining System	40
12	Sulfuric Acid Plant Schematic	44
13	Process Flow Diagram Tail Gas Scrubber	46
14	Project Schedule	49
15	F.G.D. System Operating Periods & Outages Jan. 1974 - June 1974	85
16	General Arrangement Plan F.G.D. System	88
17	General Arrangement Plan Regeneration System	89
18	Venturi Throat Area Wear	98
19	Demister Modules	98
20	Recycle Pump Impeller Wear	99
21	Recycle Pipe-Upper Section	101
22	"T" Section of Recycle Line	102
23	Cross Section of Recycle Pipe	103
24	Microstructure of Recycle Pipe I.D.	105
25	Neutralization Curve	106

FIGURE

		<u>Page</u>
26	Centrifuge Conveyor Wear	109
27	Centrifuge Conveyor Scale	109
28	Conveyor Wear Plot	110
29	SO ₂ Removal Efficiency Effect of ΔP	130
30	Dispersed Liquid Surface Area	131
31	Effect of System pH and MgSO ₄ Level on Recycle Solids Content	133
32	Calciner Operation - Effect of Mid-Kiln Temperatures & % Carbon on Bulk Density	140
33	MgO Consumption by Operating Period	142
34	Mystic #6 Daily Load Swing	149
35	Mystic #6 Seasonal Load Swing	150
36	Process Data Flow Diagram	152
37	SO ₂ Removal Efficiency	170
38	SO ₂ Inlet Concentration	171
39	SO ₂ Inlet Concentration	172
40	Boiler Load	173
41	Absorber ΔP	174
42	Absorber Inlet Temperature	175
43	MgO Slurry Temperature	176
44	Dryer Outlet Temperature	177
45	Dryer Product Temperature	178
46	Dryer Product Solids Content	179
47	Dryer Product % MgSO ₃	180
48	Dryer Product % MgSO ₄	181
49	Dryer Product % MgO	186
50	Centrifuge Feed Rate	183
51	Centrifuge Torque	184
52	Recycle Slurry Flow	185
53	Recycle Slurry Temperature	186
54	Recycle Slurry Solids	187
55	Recycle Slurry MgSO ₄ Content	188
56	Recycle Slurry MgO Content	189
57	Recycle Slurry pH	190
58	Calciner - Mid-Kiln Temperature	191
59	Calciner Feed Rate	192
60	Calciner Product - % MgO	193
61	Calciner Product - % MgSO ₄	194
62	Calciner Product Bulk Density	195
63	Calciner Off-Gas % O ₂	196

TABLES

		<u>Page</u>
1	Typical Composition at Major Product Streams	6
2	Typical Fuel Oil Analyses	28
3	Sulfuric Acid Unit Feed Gas	30
4	Stream Properties & Composition - Absorber & Centrifuge System	33
5	Stream Properties & Composition - Drying System	39
6	Stream Properties & Composition - MgO Regeneration System	41
7	Stream Properties & Composition - Tail Gas Scrubber	47
8	Absorber Gas Flow	63
9	F.G.D. System Availability by Test Program Phase	83
10	F.G.D. System Availability - June 1973 to June 1974	84
11	Equipment Performance F.G.D. Systems	90
12	Equipment Performance Regeneration System	93
13	Chloride Analyses	97
14	Centrifuge Operating Hours	108
15	Stack Drainings Analyses	112
16	Corrosion Test Data	115
17	Coated Specimen Test Coupons	117
18	Calciner Product Screen Analyses	123
19	Effect of Temperature of Digestion on SO ₂ Removal Capacity	124
20	Rate of Hydration of MgO	125
21	pK Values of Weak Acids	126
22	Potential Sources of MgO Losses	143
23	SO ₂ Removal - Performance Test Results	155
24	Particulate Removal-Performance Test Results	156
25	Particulate Removal by Particle Size Performance Test Results	157
26	Oil Analysis During Performance Tests	158
27	F.G.D. System Operating Conditions	161
28	F.G.D. System Stream Analysis	163
29	Regeneration System Operating Conditions	165
30	Regeneration System Stream Analysis	167
31	Mystic #6 Boiler - Fuel Oil % Sulfur	198

TABLES

	<u>Page</u>
32 High Sulfur Oil Ash Analyses	200
33 Regenerated MgO - Vanadium & Nickel Content	201
34 Summary of Financial Data	203
35 System Cost Details - F.G.D. Plant	204
36 System Cost Details - Regeneration Plant	205
37 Operating Cost - F.G.D. Plant	207
38 Operating Cost - Regeneration Plant plus Testing & Quality Control Program	208
39 Project Management Costs	211
40 Summary of Estimated Final Investment - 200 MW Coal-Fired Unit	214
41 Annual Costs - 98% H ₂ SO ₄ From Power Plant Stack Gas - 200 MW Coal-Fired Unit	215

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1.0 SUMMARY

The control of emissions from fossil fuel fired equipment has long been a matter of national concern. Of these pollutants sulfur dioxide (SO_2) produced in the combustion of coal and oil at power generating plants represents approximately 55% of the SO_2 discharged annually to the natural environment in the United States.

Acting under the impetus of the Clean Air Act to reduce SO_2 emissions and establish air quality standards several methods of control for this pollutant were implemented. Initially, reduction of SO_2 levels was accomplished through the use of low sulfur fuels. However, because of their limited availability and high costs, the significant impact on abatement of SO_2 emissions is expected to come from flue gas desulfurization (F.G.D.) methods.

The F.G.D. processes are generally divided into two categories: "throw away" and "regenerable". In the throw away processes, flue gas SO_2 is absorbed, precipitated as a sulfur containing solid material and the solid is disposed of as a waste material. In the regenerable processes, the SO_2 is absorbed and subsequently recovered in a usable form while the absorbent is regenerated and returned to the F.G.D. system.

One regenerable flue gas desulfurization process is based upon the reaction of magnesium oxide (magnesia) with SO_2 , forming magnesium sulfite. The magnesium sulfite solids are separated by centrifugation, dried to remove moisture and then calcined to regenerate magnesium oxide for recycle and SO_2 for conversion into sulfuric acid. Once properly conditioned, the SO_2 can be used by existing as well as new sulfuric acid plants.

Although laboratory and pilot work had been done by Chemical Construction Corp. on the absorption and integrated plant operation and by Basic Chemicals on the regeneration steps by 1970 several questions on full-scale application of this method remained.

- 1) The ability to efficiently remove sulfur oxides from the flue gases.
- 2) The ability to continually regenerate a reactive magnesium oxide.
- 3) The quality of the product sulfuric acid.
- 4) Mechanical and materials reliability.
- 5) Projected construction and operating costs.
- 6) Transport and storage properties of the magnesium sulfite and regenerated magnesium oxide.

In 1970, the U.S. Environmental Protection Agency and the Boston Edison Company agreed to provide the funds for the construction and 2-year operation of a large prototype sulfur dioxide recovery plant based upon magnesia slurry scrubbing. The Chemico-Basic magnesia process was chosen. The SO₂ absorption plant was installed at Boston Edison's Mystic Station in Everett, Massachusetts, and the regeneration facility at Essex Chemical's Rumford, Rhode Island, sulfuric acid plant. The process was scaled up from a small pilot plant handling 1,500 cubic feet per minute (CFM) of gas to a full size unit designed to treat the flue gas (450,000 ACFM) from a 150 MW generator at the station fired with high sulfur, No. 6 fuel oil.

A test plan was developed to answer the questions on full-scale system performance, and to determine the effects of the numerous control and stream composition variables on operability and efficiency of the magnesia slurry method of SO₂ control. The goals of the program were achieved and relationships developed to measure the effect of variations in system operation on both SO₂ removal efficiency and absorbent regenerability.

The program spanned a 21 month period for construction of the plants and a 27 month period of operations divided into a preliminary pre-startup and shakedown period, planned operational testing period and an end period for continuous

running at a stable set of conditions. In all, over 4,000 hours of running time of the F.G.D. system were logged.

1.1 BOSTON EDISON SO₂ RECOVERY

The chemical and mechanical performance of the scrubber itself was excellent. None of the internal plugging problems which plagued the early operations of the lime and limestone processes were encountered. The plastic lining of the scrubber was in sound condition after two years of operation. Erosion and corrosion were experienced in the carbon steel recirculating slurry piping. The use of rubber-lined pumps, valves, and piping in certain areas of this system is now considered as the most practical solution to this problem. The SO₂ removal efficiency was excellent over a wide range of operation, even during the last six months of the project when the SO₂ control system faced frequent boiler outages. The results of the performance tests which were conducted by a third party, York Research, gave as an average (four tests):

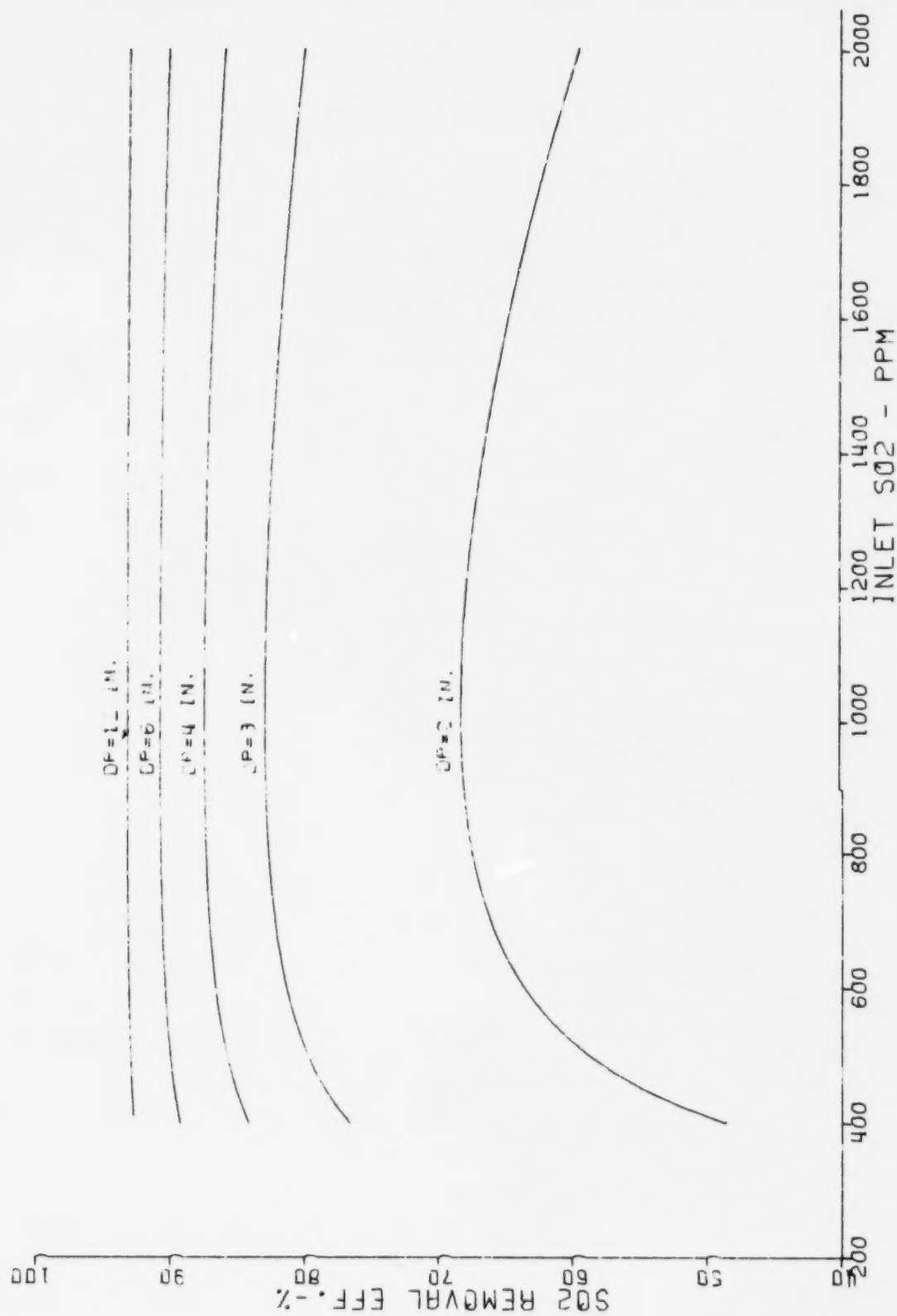
SO ₂ Removal	91.7%
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Oil Ash Particulate Matter Removal	57%
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A correlation of SO₂ removal efficiency as a function of inlet SO₂ concentration and pressure drop across the scrubber was developed based on actual performance data and the correlation is shown graphically in Figure 1. In this same figure, the excellent operability range of the system is shown by the consistently high removal efficiency curves for pressure drops above 6 inches of water.

The major control variables used to regulate the scrubbing operation were the recycle slurry pH and percent solids. The effect of pH on SO₂ concentration is shown in Figure 2. The effect was controlled by adjusting the rate of MgO addition. Typical compositions of the recirculating slurry are shown in Table 1, along with other key streams. The amount of solids in the slurry was controlled by adjusting the rate of bleed from the recycle slurry.

The majority of the operating problems experienced at the power plant installation were closely tied to the solids-handling system. Many of these problems were due to the



SO₂ REMOVAL EFFICIENCY
EFFECT OF DELTA P AND INLET SO₂ CONC.

Fig. 1



EFFECT OF PH ON SO2 OUTLET CONC. (PPM)
-BOSTON EDISON JUNE 1973

Fig. 2

TABLE 1

TYPICAL COMPOSITION OF MAJOR PRODUCT STREAMS

	% Of Total Stream			
	MgO	MgSO ₃	MgSO ₄	Water & Inerts
Recycle Slurry*	0.3	6.3	14.4	79.0
Centrifuge Cake	2.2	37.8	6.5	53.5
Calciner Feed	7.1	60.3	10.9	21.7
Calciner Product	87.1	0	7.7	5.1

*Approximately 10% suspended solids in slurry

nature of the magnesium sulfite crystals obtained from the scrubber. Although the easily separated magnesium sulfite hexahydrate ($\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$) crystals produced in the pilot operations were expected, any sustained operation of the scrubber resulted in the production of the finer magnesium sulfite trihydrate ($\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$) crystals.

This unexpected occurrence resulted in crystal properties different from those used in the design of the solids-handling system and the dryer, and was the primary process problem encountered in the project. Modifications eventually were required in all of the process areas handling magnesium sulfite crystals to allow for operation with large amounts of the trihydrate present.

The rotary dryer, used for removing free and bound water from the centrifuge slurry solids, was found to be at the center of these initial operating problems. Since this dryer was designed for operation with the relatively coarse hexahydrate crystals, the fine trihydrate crystals caused excessive dusting, buildup of solids, and loss of drying ability. The following modifications led to reliable drying:

- 1) The dryer operation and internal configuration were modified to allow the dryer to act as a granulator for the fine crystals.
- 2) A scalping screen and lump breakers were installed at the dryer discharge to handle oversize agglomerated granules of dried magnesium sulfite from the dryer.
- 3) High dust losses from the dryer because of the fine crystal size were corrected by piping the dryer off-gas to the venturi scrubber.
- 4) Hammers were installed on the dryer shell to prevent the build-up of solids.
- 5) The dryer conveyor was lengthened to allow wet centrifuge cake to be added at a point further into the dryer.

- 6) The mixing of the dry material, removed from the cyclone dust collector operating on the dryer off-gases, with the wet centrifuge solids created a mixture which would "set up" on the screw conveyor. A pneumatic conveyor system was installed to transport this material directly to the MgSO_3 silo.

As the first regenerated magnesium oxide arrived at the power plant for reuse, other problems in solids handling developed. The calcined magnesia returned from the acid plant contained a fraction of a larger-than-desirable particle size as well as some overburned MgO particles that would not react with water to form a reactive slaked slurry. A pulverizer was installed to grind this oversized MgO to that which was usable. This pulverizer was eventually transferred to the acid plant. In addition, magnesium oxide returning from the acid plant initially showed a lower reactivity than expected. This was corrected by heating the MgO slurry tank to 180°F to increase the slaking rate of the MgO .

The combined effects of corrosion and erosion were experienced in all pumps, valves, and piping that handled the scrubbing slurry. Because the prototype plant was designed for only a two year period of operation, cast iron and carbon steel were used in these areas and quickly failed. Rubber or plastic lining is now considered necessary in slurry-handling applications.

While centrifuge performance was generally satisfactory, improved internal washing techniques were required to reduce wear and improve reliability.

The availability of the SO_2 recovery system to the Boston Edison Unit No. 6 boiler ranged from a low of 13 percent to a high of 87 percent during the April 1972 and June 1974 operating periods, respectively. Many of the lower value availabilities were caused by the problems discussed above. During the last four month period of the recovery system's operation, the monthly availabilities were 87 percent, 81 percent, 57 percent and 80 percent. The lowest reported value was due to the lack of MgO for SO_2 removal, caused by problems in the sulfuric acid plant and an intentional

emptying of the MgO silos during a controlled system test.

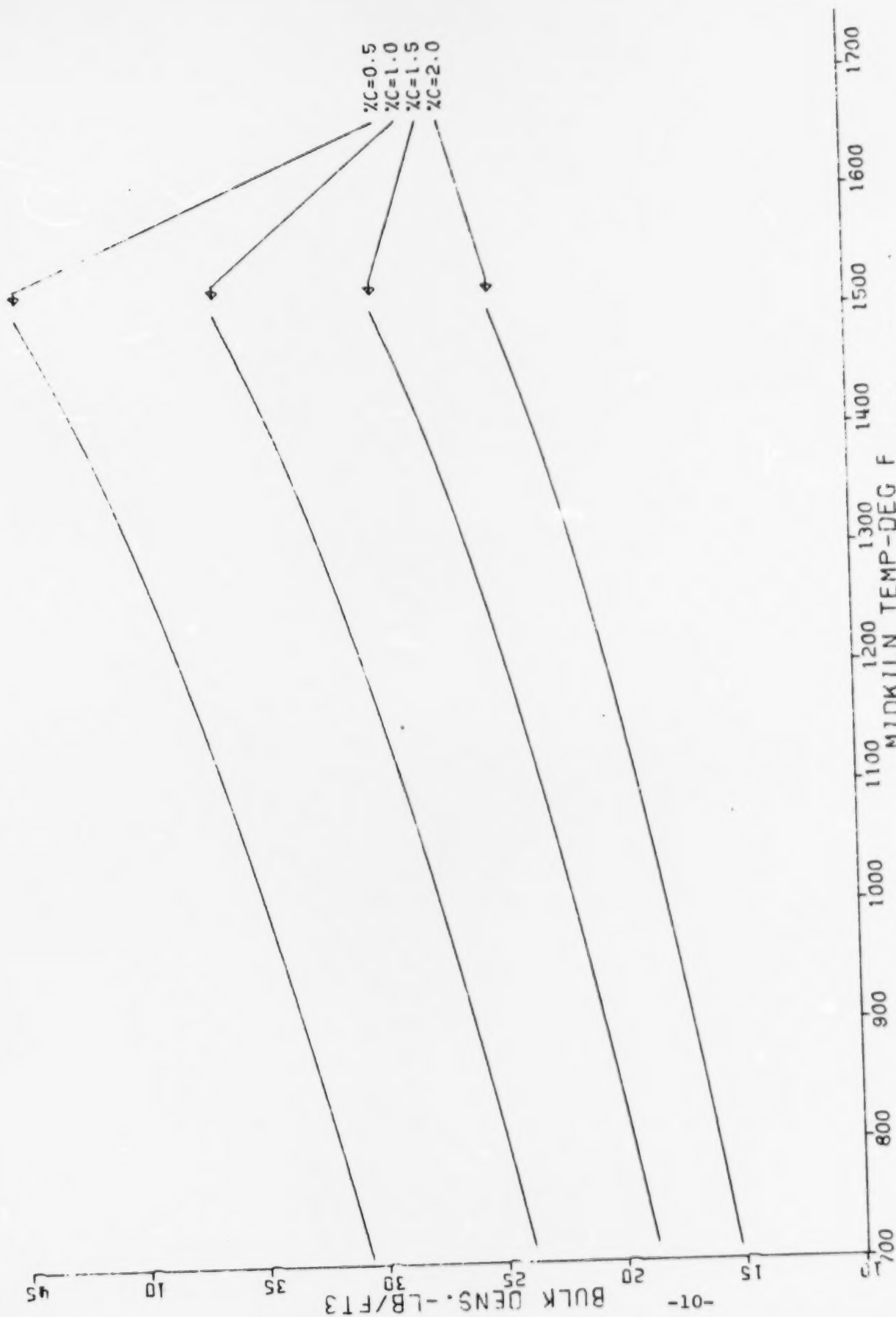
1.2 ESSEX CHEMICAL - MgO REGENERATION AND SULFURIC ACID PRODUCTION

After solving several initial operating problems, which are discussed in the following paragraphs, the chemical plant was consistently able to manufacture high quality 98 percent sulfuric acid, which was sold in the commercial market. Over 5,000 tons of H_2SO_4 were made from captured flue gas sulfur. During this same period, 3,000 tons of magnesium oxide were regenerated and shipped to the power plant for reuse.

The continued ability of the system to operate efficiently with regenerated magnesium oxide was a major variable investigated during the project. The occasional formation of a small amount of less reactive MgO was observed. This was generally accompanied by an increase in density of the magnesia. Data from this test program were correlated by regression analysis with operating conditions and the percentage of carbon in the feed to predict operating conditions which would result in a low-bulk-density magnesia. This correlation is shown in Figure 3 and indicates that the formation of low-bulk-density (high reactivity) magnesia is favored by low calciner temperature and an increased amount of carbon in the calciner feed.

Mechanical problems at the chemical plant were centered around the calciner operation. One such problem was air leakage into the calciner's firing hood. The calciner must operate at very near neutral or reducing conditions in order to allow for the reduction of magnesium sulfate to magnesia. A considerable amount of effort was expended in tightening up seals and reducing air leakage. The problem was finally solved by the installation of a friction seal.

Another problem occurred when oil was fired during the startup of the cold calciner. Hydrocarbon vapors not removed by the scrubbing equipment entered the sulfuric acid towers, which immediately caused blackening of the acid. This problem was solved by installing a fan and a short stack, which allowed the startup vapors to bypass the sulfuric acid plant.



CALCINER OPERATION - EFFECT OF
MIDKILN TEMP. & %C. ON BULK DENSITY

Fig. 3

This system was used only when heating up the calciner and was never operated during periods of SO₂ generation.

1.3 MgO LOSSES

During the early period of operation, magnesium oxide losses were excessive due primarily to spills and required cleanouts caused, as previously described, by the solids-handling problems.

1.3.1 Boston Edison

In the final four months of operation, however, the bulk of these problems were solved and a careful measurement was made of system losses. During these four months, 1,500,000 Pounds of regenerated material were recycled to the power plant as scrubber slurry makeup. A 13-day test to identify each specific loss point was also conducted. The measurements showed a loss over the entire power plant operation of 0.37 ton per operating day, distributed as follows:

Loss to stack	0.13 ton per day
Scrubber overflow	0.14 ton per day
Miscellaneous	0.10 ton per day
Total	0.37 ton per day

With an average MgO consumption of 10.61 tons per day during this period, this total loss amounted to 3.5 percent of MgO consumption at the power plant. The design loss at this same location was predicted to be 5 percent.

1.3.2 Essex Chemical

The greatest losses for this project occurred at the regeneration plant in Rumford, where 0.5 ton per day was scalped off the calciner product as large lumps before the pulverization process. Future system design will provide for the reclaiming of these losses. In addition, 1.5 tons per day were lost from the neutralizer overflow. In subsequent designs, this large loss can be recovered for recycle by separation of solids in the neutralizer overflow. Thus,

almost all of the regeneration plant losses can be reclaimed by improved design at new regeneration plants.

1.4 GENERAL

Operation of the full size plant yielded much valuable information for the design of future plants. During the course of this project:

*

1) Studies of the complex physico-chemistry of the process were undertaken yielding data not previously reported on:

a) The kinetics of the MgSO_3 hydrate formation and transformation.

b) The activation phenomena of regenerated MgO slaking.

c) The formation and influence of MgSO_4 in the system.

2) Measurements were made of the physical properties of the chemical components of the system.

3) New analytical methods and techniques were developed to assure process and quality control at the plants.

4) Observation and testing of the suitability of the equipment and materials of construction yielded new recommendations for the design of improved plants.

Finally, the accumulation of operating experience and a large data bank for reference allowed initiation of the second phase of the overall application of the magnesia slurry system for SO_2 control at a coal fired generating station.

* Work in these areas is still ongoing.

2.0 BACKGROUND AND INTRODUCTION

The control of sulfur oxides emitted to the atmosphere from power plants has become increasingly important in recent years. The deleterious effect on human health and the environment of these substances has been well documented and needs no review here. The growing demand for energy has compounded the problems of pollution abatement. For example, total SO₂ emissions in 1965 were estimated at 25 million tons per year, and it was anticipated that, if no controls were imposed, these emissions would rise to 75 million tons per year in the United States by 1975. Of this amount, two thirds would originate from the products of combustion of fossil fuel fired power stations.

The national concern for this and other problems related to air pollution was reflected by the Congress initially in the authorization of a Federal program of research for air pollution control in 1955, the later adoption of the Clean Air Act of 1963, and finally the Air Quality Acts of 1967 and 1970. All of these acts focused attention on the environmental problems created by the conversion of fossil fuels to energy for heat and power. Also reacting to these problems, the utilities and chemical industries instituted numerous programs and studies for environmental protection, many industries having installed pollution abatement equipment decades before the enactment of the specific legislation.

Chemico, a leader in the field of the design and construction of air pollution control equipment and in the incorporation of environmental protection provisions in the chemical plants which it also designs and constructs, drew on its 27 years experience in particulate emissions control and initiated several in-house studies in means of SO₂ control from large boilers. By 1966 these Chemico marketing studies indicated that the New England area would become a high cost area for fuel oil and that low sulfur content fuel, then proposed as the solution for SO₂ emissions, would itself have the highest cost impact. Engineering studies had also revealed that alternative schemes for SO₂ control which produced waste products were unacceptable in the New

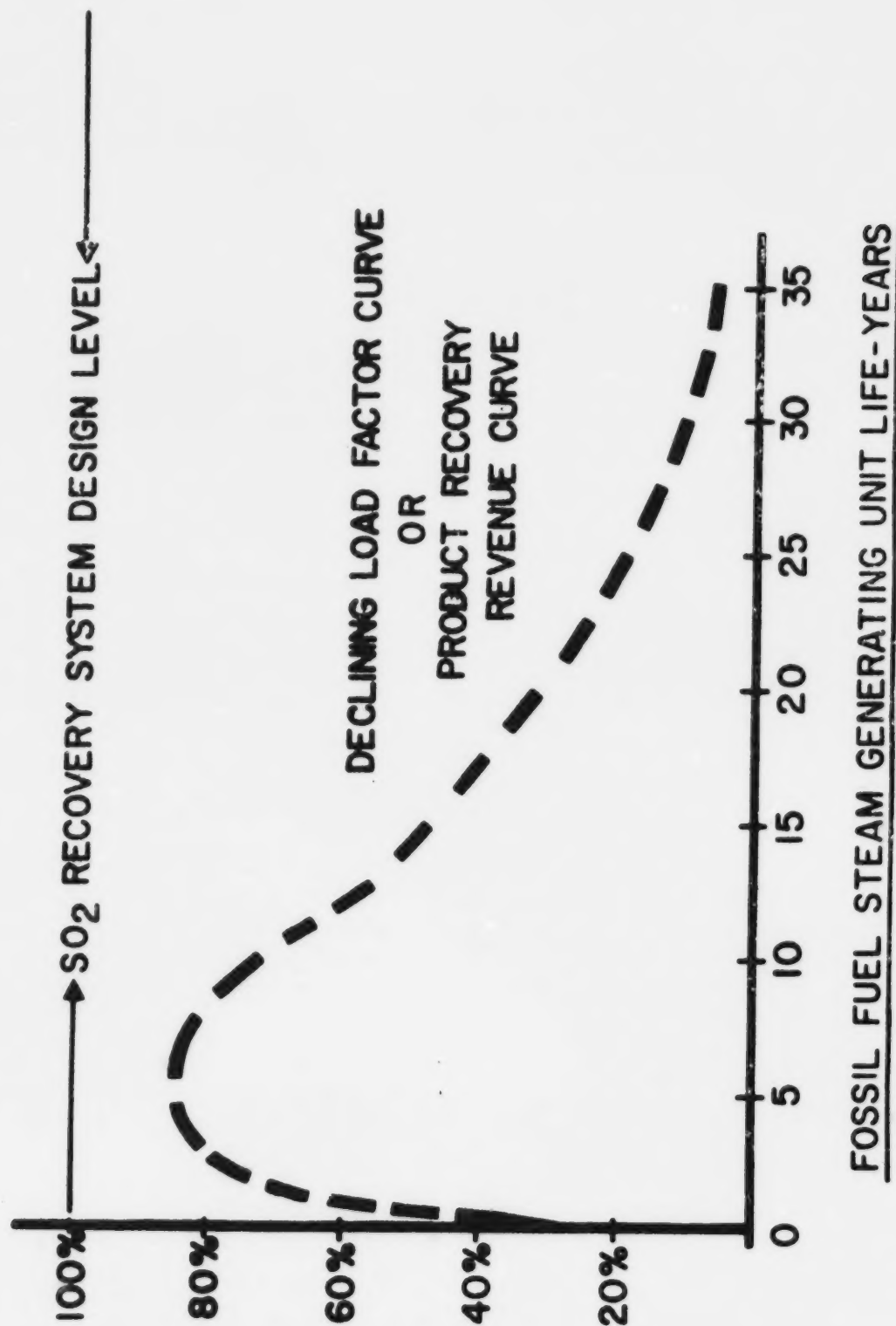
England area due to the lack of disposal sites. Evaluating this information, laboratory studies were initiated on methods of controlling emissions by the use of a regenerable process. These studies demonstrated that a process built on the use of magnesia appeared to be the most practical. In addition, the magnesia system provided a means of incorporating the concept of a separate, self-contained, central regeneration plant to serve many power plants. This chemical plant could then be sized economically for the recovery of sulfur values, and the design could be based on the longer, full production capabilities of such plants, rather than the diminishing power production (Fig.4) experienced in modern generating stations.

An incentive for rapidly proceeding to full scale plant operations of the magnesia process, by-passing the smaller scale semi-works units normally employed in scale-up, was provided by the Panel on Control of Sulfur Dioxide from Stationary Combustion Sources. This panel, a committee of the National Research Council and the National Academy of Engineering, had recommended funding of prototype facilities in order to speed the demonstration of the necessary pollution abatement systems.

The arrangements for funding the magnesia system prototype were concluded in a master contract signed in June, 1970. In it the United States Environmental Protection Agency and Boston Edison Company agreed to provide the funds for a large prototype system using the Chemico-Basic MgO Sulfur Recovery Process for control of SO_2 emissions from power plants.

Capital funds for the absorption system to be installed at the power plant were provided by the Boston Edison Company, while E.P.A. furnished funds for the magnesium oxide regeneration system to be installed at a small sulfuric acid plant located in Rumford, R.I., owned by Essex Chemical Company, as well as the acid plant modifications necessary to accommodate a "roaster gas" process. Operation and maintenance of the facilities were the responsibility of Essex Chemical Company and Boston Edison Company, respectively, with reimbursement of these costs by E.P.A. However, Boston Edison's reimbursement was limited by a ceiling. Chemico was responsible for Project Management of the total project, with a part of the

FIG. 4 - THE EFFECT OF LOAD FACTOR
UPON SO₂ RECOVERY REVENUE



cost reimbursed by E.P.A.

A history of these and the subsequent events which led to the full scale demonstration of the magnesia process on a utility boiler is summarized below:

NEW ENGLAND SO₂ CONTROL PROJECT HISTORY

- 1966 - Chemico studies showed New England would become a high fuel oil cost area.
- 1966 - Boston Edison was investigating alternatives to the use of low sulfur fuel.
- 1967 - Laboratory studies of SO₂ removal/regeneration schemes were initiated by Chemico.
- 1967 - Chemico and Boston Edison Co. discussed testing of these schemes at a Boston Edison Co. generating station.
- 1968 - Pilot plant studies of the magnesia system at generating stations were undertaken by Chemico.
- 1969 - Chemico and the Environmental Protection Agency discussed mutual funding and participation in a demonstration project.
- 1970 -
 - 1) The master contract, creating the New England SO₂ Control Project was signed by Chemico, Boston Edison Co., and E.P.A.
 - 2) Chemico entered into agreements with Boston Edison Co. for the design and erection of a magnesia system in their Mystic #6 boiler.
 - 3) Chemico and Essex Chemical Co. entered an agreement whereby the regeneration

section of the magnesia system would be erected at their Rumford, R.I. sulfuric acid plant, and the recovered SO_2 would be processed into sulfuric acid.

4) Chemico completed process and design engineering for both plants.

- 1971 - Construction of both plants started.
- 1972 - Construction of both plants completed.
- 1972 - Initiation of the start-up phase of the New England SO_2 Control Project Test and Development Program.
- 1973 - Initiation of the Planned Operational testing phase of the program.
- 1974 - Completion of the program.

This report covers the period from January 1st, 1972 thru the end of the project on June 30th, 1974. During the first few months of this period, construction at Mystic Station was completed. This completion had been delayed from the original forecast date of October 1971 to April 1972 because of a combination of cold weather, competing maintenance projects at the same station, and a lower productivity in the area than had been predicted.

During the following two year period, the operations and test work was conducted, again with an altered schedule.

The pre start-up period originally scheduled for two weeks was extended to three months as methods were developed to cope with the different hydrate and crystal size of magnesium sulfite which was produced in the continuous operation, as this material had not been encountered in the previous intermittent pilot plant operation. The Start-up Shakedown Phase scheduled for a three to six month period was not completed till the end of April 1973 because of the step-wise

system necessary to solve the numerous operational, mechanical and materials handling problems that arose as the work progressed.

The planned operational test period was shortened and concluded by February of 1974. At this time, performance tests were run on the system, and these demonstrated satisfactory compliance with guarantees. After the performance tests were completed, the period from March 1974 to the termination of the project was devoted to longer and steadier operational periods at both plants.

Description of the work performed in the previous period during most of the construction phase, complete engineering designs of the system, and extensive descriptions of the operational programs, have been presented in the following reports:

- 1) Detailed Engineering Report
Contract CPA 70-114; Chemico Job 1857G
- 2) Detailed Engineering Report
Contract CPA 70-114; Chemico Job 1858G
- 3) Report for the period 7/1/70 thru 1/1/72
Contract CPA 70-114
- 4) Test and Development Program
150 MW Prototype Venturi Scrubbing System
- 5) Planned Operational Test for New England SO₂
Control Project

3.0 GENERAL PROCESS DESCRIPTION

Chemico/Basic's Magnesium Oxide System for the recovery of sulfur dioxide from power plant flue gases is shown schematically in Figure 5. This process, which utilizes the sulfur dioxide absorption characteristics of an aqueous slurry of magnesium sulfite, magnesium sulfate, and magnesium oxide, is composed of five primary steps, these are:

Absorption
Centrifuging
Drying
Materials Handling
Calcination

a) Absorption

The process chemistry which describes the removal of SO₂ from the flue gas can be most simply explained as the diffusion of SO₂ through the flue gas to a liquid surface, absorption of the SO₂ gas in the liquid and the subsequent reaction of SO₂ with the hydrated form of MgO, i.e.

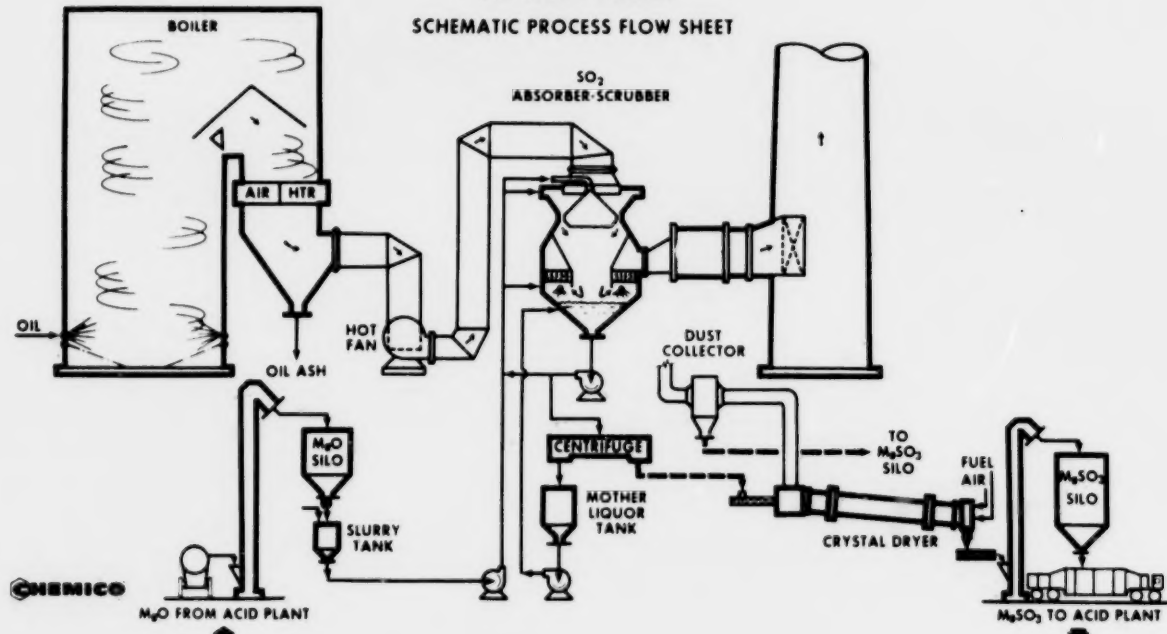


The MgSO₃ produced has a low solubility and can be separated from the absorbing slurry as a solid.

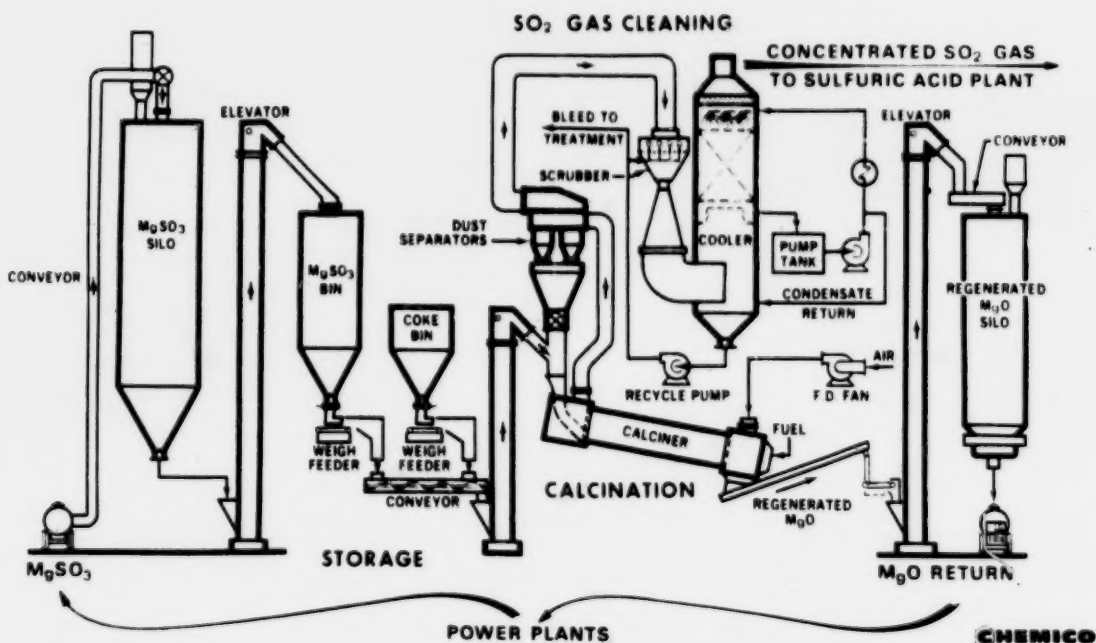
In the process the flue gas containing sulfur oxides enters a venturi absorber (Figure 6) of special design, and contacts the absorbing media which is an aqueous slurry of magnesium oxide, magnesium sulfite, magnesium sulfate, and a small percentage of other components including fly ash from the fuel oil. The process of SO₂ removal that occurs is explained by conventional mass transfer principles.

The venturi absorber can be considered as similar to a co-current, packed vessel. In the venturi the liquid slurry is introduced and flows downward on surfaces over which pass an accelerating gas stream. The high velocity gas stream flowing over the liquid causes wave motion on

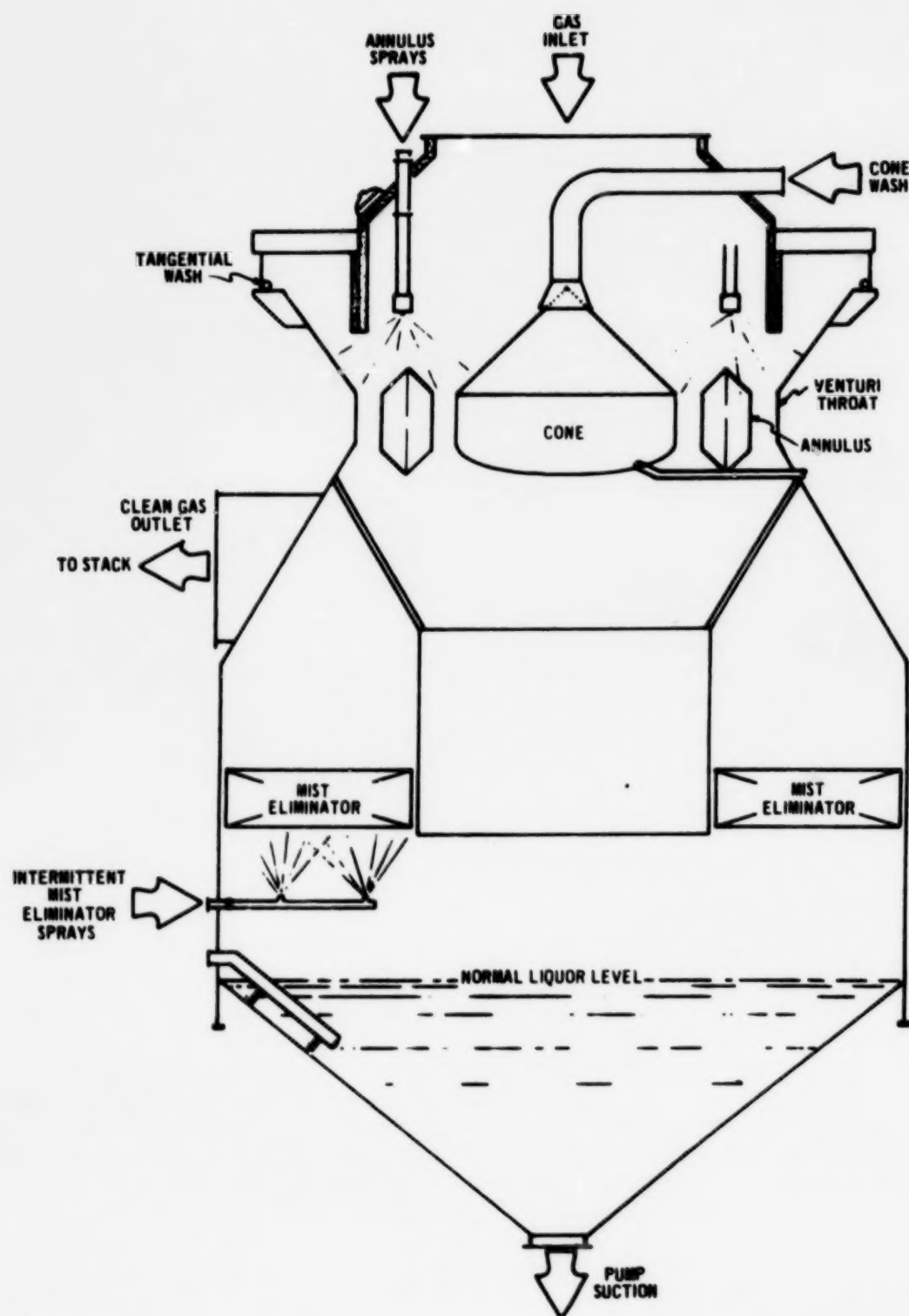
MgO ADDITIVE SCRUBBER SYSTEM FOR SO₂ RECOVERY OIL FIRED BOILER



REGENERATION SYSTEM **MgO RECYCLE PROCESS, FOR PRODUCTION OF 98% SULFURIC ACID** SCHEMATIC PROCESS FLOW SHEET



Magnesia Flue Gas Desulfurization and Regeneration System
Schematic Flow Diagram



Sectional view of absorber at Boston Edison Company, Boston, Mass.

the fluid surface, the waves increase in amplitude and finally disperse as fine droplets. Thus, the whole mass of liquid can be distributed in the form of atomized droplets in the gas stream. In the process described in this report, the dispersed droplets generally have a median size of 400 micrometers and the surface area available for mass transfer averages 13 ft² per ft³ of gas.

There are several advantages in using the venturi as an absorber: The absorption surface is dispersed into and flows with the gas stream during the time absorption is occurring, thus eliminating the problems of plugging associated with conventional packed towers (the surface area per unit volume is approximately equivalent to dumped 3 inch rachig rings). Due to system dynamics, this surface area relation is relatively invariant over wide turn-down ratios, and high removal efficiencies can be maintained over the normal operating range of the power plant's boiler.

A prediction of system efficiency can be obtained with a fair degree of accuracy by assuming a pure diffusion phenomena and conventional mass transfer relations. Using this as an estimate, a maximum efficiency of 96% is possible for a single stage system. Deviations from that removal efficiency in the demonstration plant and primarily caused by equilibrium partial pressures of SO₂ over the droplet surfaces greater than zero in the dynamic system.

b) Centrifuging

A stream from the absorption system enters the centrifuge where the solids which were formed by the absorption reaction in the slurry are separated. This bleed stream is controlled in order to maintain a constant solids content in the recycle slurry by removal of product magnesium sulfite and unreacted magnesium oxide and any precipitated magnesium sulfate. The system is operated so that the absorbed SO₂ is removed as an equivalent amount of the magnesium sulfur compounds.

c) Dryer System

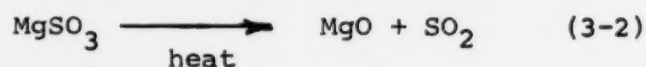
The wet centrifuge cake containing hydrated magnesium sulfite, magnesium oxide and magnesium sulfate plus other solids removed in the venturi absorber-centrifuge system is passed to a rotary dryer to remove both unbound water and most of the water of crystallization. The dry product is easy to store, and the removal of water reduces shipping costs.

d) Materials Handling

The anhydrous magnesium sulfite and magnesium sulfate produced in the dryer is conveyed to a storage silo for transportation by truck to the recovery acid plant. The same transportation equipment is used to return regenerated magnesia to the magnesium oxide silo at the power plant on the return trip. Recycled alkali absorbant from the magnesium oxide silo and make-up magnesium oxide are fed to an agitated tank with water where a slurry is prepared for introduction to the recycle system manually on pH control.

e) Calcination System

Calcination is the process for the regeneration, which is the reverse of the absorption step. The magnesium sulfite which has been separated and dried is thermally decomposed as represented by the following reaction:



The recovered SO_2 is used in the production of sulfuric acid and the regenerated MgO returned to the process for reuse. The dry product transported to the regeneration acid plant from the power plant is received, weighed and pneumatically conveyed to a storage silo. It is fed to a direct-fired rotary kiln at a metered rate, and calcined to both generate sulfur dioxide gas and regenerate magnesium oxide. Coke can be added to provide a reducing atmosphere, as necessary, to reduce the residual magnesium sulfate to the oxide and sulfur dioxide. The hot

flue gas containing sulfur dioxide and dust enters a hot cyclone where essentially all the dust is removed and returned to the calciner. The flue gas then enters a venturi scrubber for final dust cleaning. At the same time, the gas is cooled and adiabatically saturated.

The saturated flue gas is cooled in a direct contact cooler to meet the requirements of the acid plant water balance. The cleaned, cooled flue gas then enters the drying tower of an existing 50T/D acid plant. At the Essex Chemicals installation, the resultant product made from the recovery of the sulfur dioxide is 98% sulfuric acid.

The regenerated magnesia is cooled, conveyed to the magnesia storage silo and recycled back to the power plant.

3.1 DESCRIPTION OF INSTALLATIONS

The magnesia method of flue gas desulfurization removes SO_2 from the products of combustion of fossil-fuel fired equipment by absorption in a slurry containing the alkaline material, magnesium oxide. In subsequent steps the SO_2 is driven off by a thermal decomposition of the solid products of absorption regenerating the magnesia for reuse. Variations in the process can be used to obtain a range of strengths of SO_2 in the gas from the thermal decomposition so that the products of the recovery operation can vary from elemental sulfur or sulfur dioxide to sulfuric acid. In the work described in this report the flue gas to be treated came from an oil fired power boiler of an electric generating station, and the sulfur dioxide was recovered as sulfuric acid at a remote sulfuric acid plant. The power station and the acid plant are described in the following sections.

3.1.1. Power Plant

The flue gas desulfurization system was installed at the Mystic Station of the Boston Edison Company. Mystic Station is located in Everett, Mass. on a 42 acre site on the north bank of the Mystic River. The station currently includes six fossil-fuel steam electric generating units with a total

generating capacity of 618 MW and a seventh unit, under construction, with a capacity of 600 MW. The existing 618 MW capacity is provided by three 50 MW units and three 156 MW units. Flue gas from the three 50 MW units is dispersed through two stacks 278 feet high and the three 156 MW units have individual stacks 335 feet high. The units were constructed between 1943 and 1961, the last unit (No.6) beginning commercial operation in May 1961. All units were initially designed for coal firing and were equipped with electrostatic precipitators for that fuel. The station was completely converted to oil firing by 1966, and the precipitators were deenergized because of the inefficiency of particulate removal resulting from the change.

The magnesia system was installed on Unit No. 6 at the station. This generator is powered by a Combustion Engineering controlled circulation tangentially fired boiler (Fig. 7). This boiler has a rating of 1,000,000 lb /hr of steam at 1800 PSIG and 1000°F with reheat to 1000°F.

New ducting was installed at the stack breaching with dampers in the breaching to divert the flue gas from the stack to the scrubber system fans; the treated flue gas then passed back to the stack through a new breaching, also equipped with a damper (Fig.8). During most of the period of performance when the scrubber was operated it treated all of the flue gas (about 40% over design flow at full boiler loads) which was diverted by fully closing the stack inlet dampers. During the last three months of operation, the damper arrangement allowed the excess flue gas to be bypassed directly to the stack allowing the scrubber to operate closer to its design capacity and providing reheat to the combined stack gas.

The fuel oil which was burned at Mystic Station in boilers 1, 2, 3, 4 and 5 had a maximum of 0.5% sulfur as required by Massachusetts Law. For the purposes of the Test and Development program, a special variance was obtained on October 20, 1970 permitting the use of higher sulfur oil in the No. 6 unit during the periods of scrubber operation. A typical analysis of the higher sulfur oil used during scrubber operating is shown in Table 2.

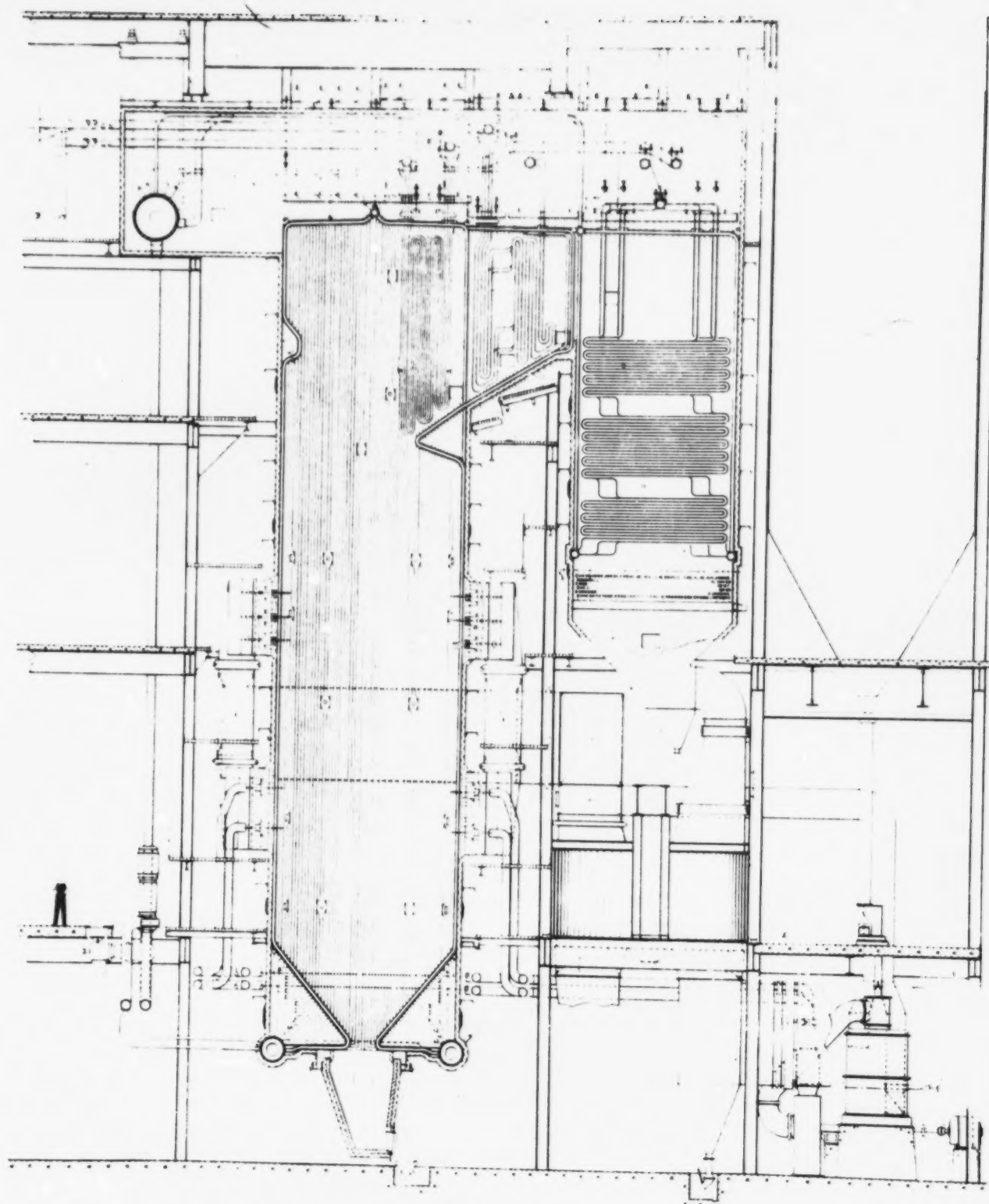


FIG. 7

C-E CONTROLLED CIRCULATION BOILER

CAPACITY: 935,000 LB PER HR AT 1000 PSI AND 1000 F TEMP - REHEAT TO 1000 F

Designed and Built by COMBUSTION ENGINEERING INC. New York

M/S IC STATION - UNITS 4 & 5 & 6

Boston Edison Company, Everett, Mass.

1000 PSI & 1000 F TEMP - REHEAT TO 1000 F

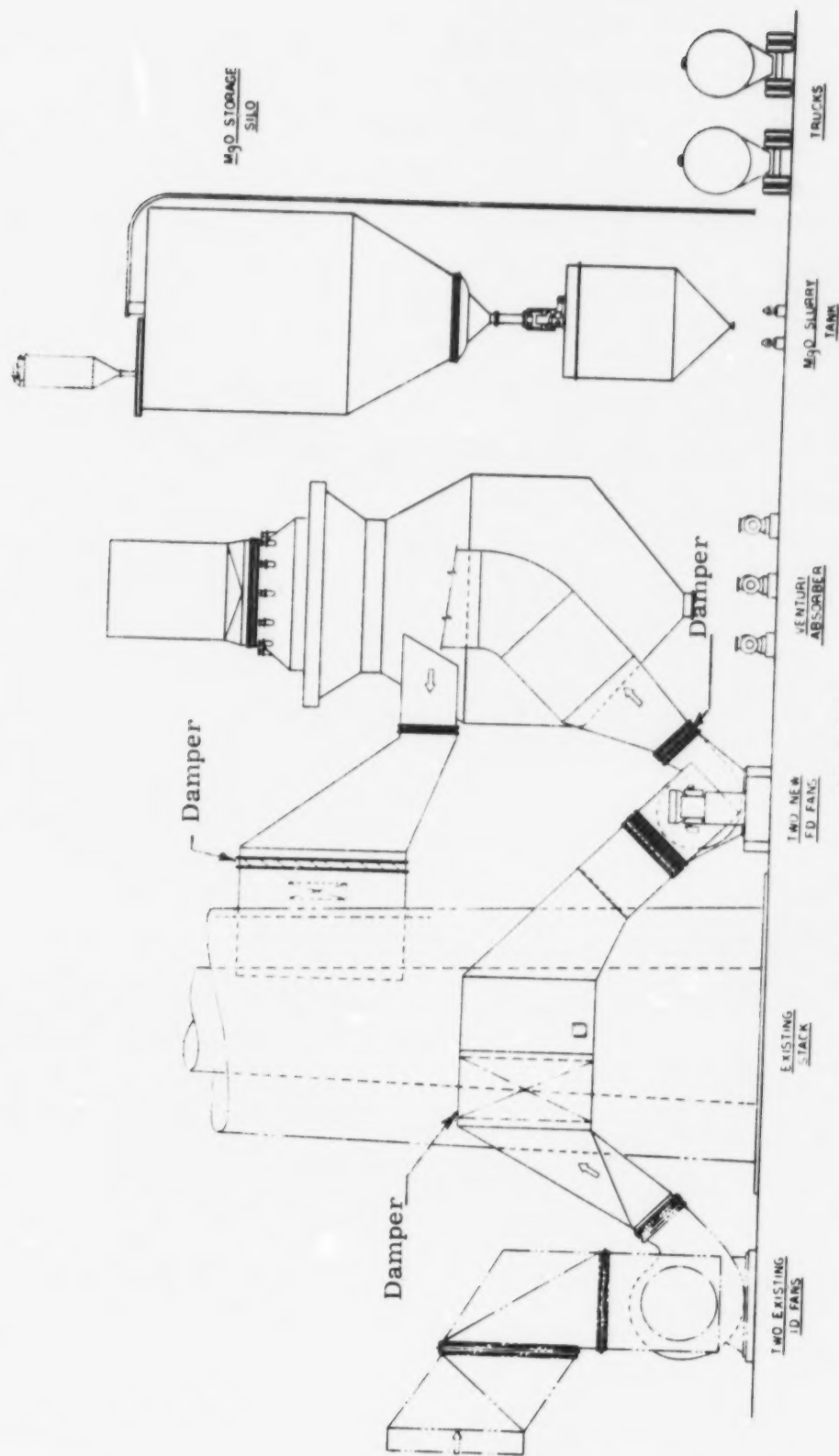


FIG. 8
 DAMPER LOCATION & DUCTS
 FLUE GAS DESULFURIZATION SYSTEM
 MYSTIC 6 STATION OF
 BOSTON EDISON CO.

TABLE 2
TYPICAL FUEL OIL ANALYSIS

Sulfur	2.05%
Ash	.07%
Carbon	84.39
Hydrogen	11.39
Nitrogen	.10
Oxygen	2.00
BTU/lb.	18,350

3.1.2 Acid Plant

The regeneration system was installed at the Rumford acid plant of Essex Chemical Company located in Rumford, RI. The Rumford plant is located 55 miles from the installation at Mystic Station and haulage of the dryer and calciner products between these two sites was done by truck. Both plants were equipped to load their respective products from elevated silos and receive their feed by pneumatic unloading. Freight rates for this haulage were established at 21 cents/cwt on a round trip basis and 35 cents/cwt for one way transport.

The plant has been producing sulfuric acid since 1929 when it was build by Chemical Construction Corporation, and

for the past several years all acid produced was sold in the merchant market with no captive use. Markets for the acid made at this plant are manufacture of detergents, dye-stuffs, pharmaceuticals, aluminum sulfate, and tanning chemicals, steel pickling, boiler water treatment, lead-acid batteries, galvanization, etc. Sales in this market were at the full published price, at the time of this program, approximately \$46 per ton based on 100% H_2SO_4 . No change in use or pricing was imposed when marketing the acid produced from MgO regeneration.

The plant is a contact sulfuric acid plant which uses sulfur as raw material. In the Chemico process the molten sulfur is injected into the furnace using a spray burner, with the process air first dried in a tower against 93% sulfuric acid. The catalyst is vanadium pentoxide.

When first built in 1928 the Rumford plant was an indoor plant typical of its time and had a capacity of about 20 tons per day of 100% sulfuric acid. Substantial modifications were made to the plant in 1948 by Chemico to increase its capacity to 50 tons per day. The modifications included improved converters, a converter heat exchanger, waste heat boiler and economizer all installed outdoors. In addition, the cast iron cooling section was enlarged and moved outside.

This was the plant that was modified in 1971 to accept the calciner off gas essentially converting it to a metallurgical (roaster) gas plant; however, in the modification the capability to continue to burn sulfur and augment the SO_2 from the regeneration plant was retained.

Typical feed gas analyses to the acid unit are shown in the following table.

TABLE 3

SULFURIC ACID UNIT FEED GAS

COMPOSITION, MOLE %

<u>Source of Gas</u>	<u>N₂</u>	<u>CO₂</u>	<u>O₂</u>	<u>H₂O</u>	<u>SO₂</u>
Regeneration Section	73	6	5	7	9
Sulfur Burning	79		12		9

3.2 DESCRIPTION OF INSTALLED FACILITIES

The pollution abatement facility, comprising the absorption, centrifuging and drying section is installed on the #6 boiler of the Mystic Station, while the regeneration plant (calcining section) is installed at the acid plant, located approximately 50 miles away. By performing the drying step at the generating station unbound water and water of crystallization are removed from the solid prior to transportation in order to reduce shipping costs.

Transportation of MgSO_3 and regenerated MgO between the two sites was handled by conventional pneumatic discharge hopper trucks. Originally two 825 ft³ units were in service however, this was eventually reduced to one 1200 ft³ trailer hauling MgO from the regeneration facility and MgSO_3 on the return trip. The tractor used had a self-contained blower for unloading material; an auxiliary compressor was available at the calcining facility to allow the trailer to be dropped completely if necessary. This compressor was also used to unload coke brought to the regeneration facility in a PD (Pneumatic Discharge) hopper rail car which was leased for this service.

During periods of extended operation of the plants, the single trailer was unable to transport all the MgSO_3 produced. In order to move the additional material necessary for uninterrupted plant operations, a local chemical trucking company provided additional units for the service. In addition, make-up MgO shipped by rail was transferred to

this same company's trucks for delivery to the power plant.

All silos, materials handling, and transport systems were designed on the basis of the bulk densities of MgO and MgSO_3 determined in preceding pilot plant work, those were 25 lb/ft^3 and 50 lb/ft^3 respectively. The storage facilities at both sites were sized to ensure that they were adequate for continued operation in the event of up to a five day interruption in shipments. This duration was chosen after an evaluation of information from the Department of Transportation of both states regarding the frequency and probability of interruptions due to weather and other circumstances. Most development work on the chemistry of the process, including new analytical techniques, was conducted by Chemico personnel in a laboratory facility located at the acid plant; these chemists and technicians also performed the chemical analysis for stream assay and quality control.

3.2.1 Magnesia SO_2 Absorption System

The SO_2 Absorption System Flow Sheet is shown in Fig.9. In this system magnesia, both regenerated and make-up material, is transferred from pneumatic discharge hopper trucks to the elevated MgO storage bin through a 4 in pneumatic unloading system. The MgO bin, 1-101, is 35 ft in diameter and 42 ft high. Magnesia is fed from the silo, which is equipped with a vibrating hopper bottom, 0-102, to a 16,000 gallon capacity MgO make-up tank G-102 by an adjustable weigh feeder, 0-103, with ratio control of make-up water to make the desired MgO slurry composition. A small pre-mix tank is interposed between the weighing system and the steam heated make-up tank to act as a vapor seal. Heated magnesia slurry is added to the recycle stream by the MgO make-up pump J-101. The magnesia slurry addition rate is controlled by the operator to maintain the pH of the absorbing slurry at the desired value.

The recycle stream for the absorber is circulated at a rate of 14,000 to 15,000 GPM to provide a slurry dispersion within the vessel sufficient for the desired SO_2 removal. The absorber vessel R-201, 31 ft Dia. x 50 ft overall is supported from a structural steel tower over the recycle pumps, J201A, B and C, and each of these 350 HP pumps had

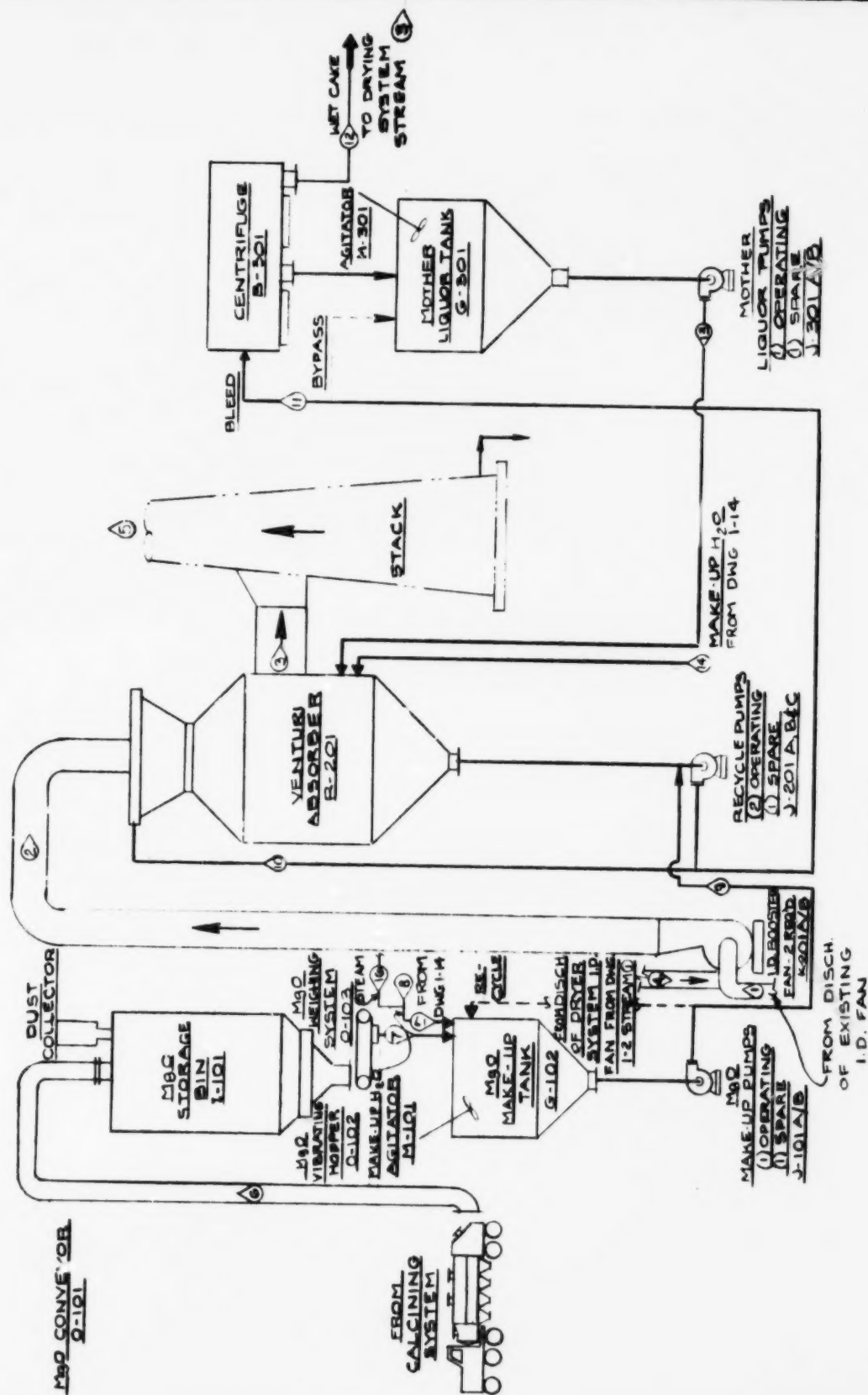


FIG. 9
SO₂ ABSORPTION SYSTEM

TABLE 4

STREAM PROPERTIES AND COMPOSITION
ABSORBER AND CENTRIFUGE SYSTEM

STREAM NUMBERS		7	8	9	10	11	12	13	14	16	17
LIQUID & SOLID STREAMS											
Temp.	F	60	180	152	132	60	180				
Flow	GPM	61	63	14600	174	64	68.4				
Solids Content	%	8.6	45.8	13.15	95.2						
MgC	lb/Min										
MgSO ₃ ·6H ₂ O	lb/Min										
MgSO ₄ ·7H ₂ O	lb/Min										
Inerts	lb/Min										
Flv Ash	lb/Min										
Total Solids	lb/Min										
H ₂ O	lb/Min										
Total Slurry	lb/Min										
Steam	lb/Min										
		507	48.1	204.5	10.7	531	570				
			555	1556.5	213.27		63				
			555								

33

STREAM NUMBERS		1	2	3	4	5
GAS STREAMS						
Temp.	°F	275	284	152	400	162
Pressure	IN WC	0	+8	+1	+1	0
Gas Flow	ACFM	423,000	439,000	378,000	20,700	411,000
Dry Gas	lb/Min	21369	22,140	22,082	771.0	22,840
H ₂ O	lb/Min	1620	1,744	2,620	174	2,692
SO ₂	lb/Min	68.2	64.0	6.4	0.8	6.8
SO ₂ PPM (Dry Basis)		1400	1,370	137		148
Flv Ash	lb/Min					.64
Mg ²⁺ S Compounds	lb/Min	0.91	0.91	5.64	1.06	0.06
Entrainment	lb/Min		1.06	540		

half the design flow of the recycle stream.

The recycle stream itself is split into three streams for distribution before reentering the venturi absorber. The flow in each stream is adjusted and set by plug valves to provide a uniform irrigation to a) the converging surfaces and b) the torroidal section of the throat area. Distribution of absorbing slurry to the torroidal section is made by 12, six inch nozzles. A similar number of tangential nozzles supply the outer converging section while the inner cone is supplied by a single central nozzle.

The slurry enters the upper part of the absorber with the untreated flue gas, which is diverted from the stack, using the dampers, through the booster fans K-201 A & B, each driven by an 800 HP motor, and each designed to handle 283,000 ACFM at a discharge head of 12 in water. The gas and slurry mixture passes through the throat area into a diverging section, then into a central downcomer to exit the vessel the flow of the cleaned flue gas turns one hundred eighty degrees upwards. In this step most of the larger liquid droplets are disengaged from the flowing gas stream and fall to the slurry pool in the conical base of the absorber. The treated flue gas continues upwards through a slot-type mist eliminator to further remove any entrained liquid before the gas exits to the stack through the louvre-type damper.

A stream of slurry, approximately 1.0% of the total recycle, is taken from the discharge of the recycle pumps to the centrifuge, R-301. This is a 36 in x 72 in horizontal, solid bowl unit driven by a 200 HP motor, and in normal operations it removes 50% of the solids in the liquid stream going to it.

The solids separated in the centrifuge contain an amount of sulphur (as MgSO_3 or MgSO_4) equivalent to the sulfur dioxide removal rate in the absorber. The centrate is discharged directly to an agitated tank, G-301 of 3,000 gallon capacity which serves as a pump tank for this system, and then is returned to the basin of the absorber by pumps J-301 A&B.

The additional water, necessary to make up for that lost

by saturation of the incoming flue gas, is also added to the basin of the absorber, and in normal operation this reservoir contains approximately 15,000 gallons of slurry. The other sources of water entering the system are small amounts added as pump seal water and an additional quantity used as a mist eliminator wash; the latter is an intermittent addition.

The flow sheet for the centrifugeing and drying section is shown in Fig. 10. The centrifuge cake separated in the centrifuge is fed to a dryer by screw conveyer 0-402, a 34 ft long unit with a 14 in diameter ribbon flight. The dryer is a countercurrent, rotary unit 7 ft 6 in in diameter by 60 ft long. Originally of conventional design, this unit was modified to suit the process as outlined in a later section. Heat is supplied from an integral 18 ft long oil fired combustion chamber at a maximum heat release rate of 25 MM BTU/hr.

The dryer off gas exits through a multiple cyclone array and the gas is discharged to the entrance of booster fan K-201 B. Then, mixed with one-half of the entering flue gas, it is cleaned of its remaining particulate loading in the venturi absorber. The cyclones are designed to remove 90% of the solids entering in the dryer off gas, and the separated solids pass through a rotary valve to enter a pneumatic conveying system discharging to the product silo. In addition, some dryer product entering the spill-back bin of the dryer is transported in the same system to the product silo.

The dryer product is discharged to MgSO_3 conveyer #1, 0-403, a 13 ft long unit with a 9 in diameter, solid flight screw. The dried solids pass through a finger-type lump crusher before entering the boot of the MgSO_3 elevator designed to handle 5 TPH of anhydrous MgSO_3 . The product is finally conveyed by MgSO_3 conveyer No.2, 0-405 (similar to 0-403, except only 6 ft long) to the MgSO_3 storage bin I-401.

The storage bin, I-401, was an existing ash storage silo of tile construction. This silo, 81 ft high and 25 ft 4 in diameter, houses the MgSO_3 conveyer, 0-403, and the pneumatic conveyor blower and dust collector in its top section. The MgSO_3 screw conveyor unloading system, and the control room and motor control center are in its bottom section. Approximately a 33 ft high section of the silo, with

a capacity of 16,000 cu ft is used for the temporary storage of MgSO_3 .

The flat bottom of this silo has four discharge openings connected in pairs to two parallel discharge screw conveyors (O-407 A&B). Each of the conveyors contain two short sections of contra-rotating 14 in helicoid flight with a center discharge to a similar unit (O-407C), which cross feeds the MgSO_3 to a center discharge located over the our-loading belt, O-408, MgSO_3 Conveyer #3.

This 103 ft long, 18 in wide rubberized belt conveyor exits the silo into an elevated gallery which carries the product MgSO_3 to the truck station where it is gravity loaded through a flexible spout to the waiting hopper truck. Oversize lumps (+3/4 in) of MgSO_3 are scalped off on an inclined screen in the discharge chute and pass to a hammer mill, MgSO_3 recycle crusher, located at grade for size reduction. The milled material is conveyed back to the belt by a continuous flow conveyor.

3.2.2 Magnesia Regeneration System

Magnesium sulfite from the absorption system is received at the regeneration facility, the regeneration section flow sheet is shown in Fig. 11. The salt is unloaded from hopper trucks to the sulfite silo I-501 through a 4 in pneumatic conveying system similar to that used for MgO at the power station. The sulfite silo was an existing tile structure, 20 ft in diameter x 60 ft high, which was water-proofed before this use. Sulfite is unloaded from this silo through a pair of inclined screw conveyors, MgSO_3 conveyors 1 and 2, O-509 and O-510, equipped with 12 in diameter helicoid flights, which carry the material from the below grade discharge spout to the boot of the MgSO_3 elevator.

This elevator, O-511, a continuous discharge unit 54 ft high, is designed to handle 9 TPH of MgSO_3 . It discharges to the MgSO_3 feed bin, G-506, a 6 ft diameter by 11 ft high vessel equipped with a vibrating bottom, which also serves as a surge bin for the weigh feeder O-514. This weigh feeder is continuously variable to a maximum capacity of 3.6 TPH and discharges to the calciner conveyor O-512, a 33 ft long horizontal unit equipped with a 9 in diameter helicoid screw

Coke is also discharged to this screw which serves to mix the two components as calciner feed prior to processing.

The coke is pneumatically conveyed to the coke feed bin O-505, 9 ft diameter x 19 ft high, which also serves as the storage bin for this material. It is metered to the calciner conveyor by a weigh feeder which is also continuously variable up to a maximum capacity of 2.5 pounds per minute. The two streams (3 & 4 of Fig. 11) enter at points 9 feet apart and mix in the remaining 22 ft section of the conveyor before reaching the calciner elevator O-513, a 43 ft high centrifugal discharge unit. This elevator feeds directly to the calciner R-501.

The calciner is a refractory lined, oil fired, rotary kiln, 7 ft 6 in ID and 120 ft long. Rotational speed is variable between 1.5 and 2 RPM using a variable diameter pulley drive, and the kiln has a slope of 3/8 in per foot. The calciner product empties into four tube coolers attached directly to the shell of the kiln. The tube coolers are equipped with internal flights to contact the existing hot regenerated magnesia with incoming air which serves as secondary combustion air in the calciner, thus cooling the calciner product before it empties to the MgO conveyor #1, O-503.

This is a 9 in diameter helicoid screw conveyor, 54½ ft long, which elevates the product from the calciner tube cooler discharge seventeen feet to an enclosure housing the MgO processing equipment. The regenerated MgO is discharged from O-503 to a magnetic pulley for tramp iron separation. The MgO then passes through a 1 in mesh vibrating screen and enters a high speed pulverizer which reduces it to the finished grind shown in Table 18.

The cleaned, cooled, and pulverized regenerated magnesia flows by gravity to the MgO elevator O-504, a continuous discharge design, 89 ft high, which brings the material to the top of the MgO storage silo where it is loaded by means of a horizontal screw conveyor (MgO Conveyor #2) O-505 equipped with a 9 in helicoid screw.

The MgO silo, I-502, 25 ft in diameter and 45 ft high,

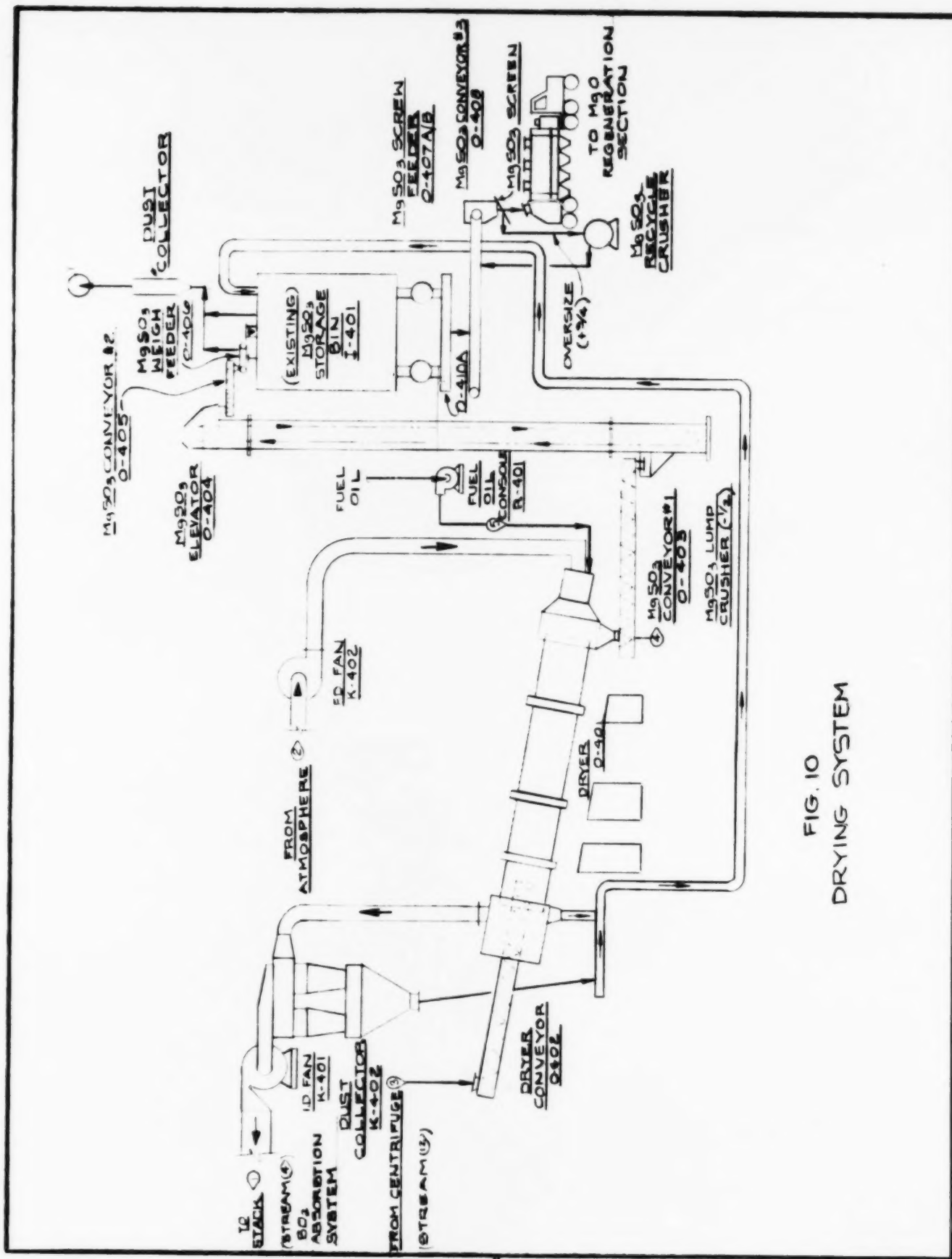


FIG. 10
DRYING SYSTEM

TABLE 5
STREAM PROPERTIES AND COMPOSITION
DRYING SYSTEM

1		2		3		4		5	
STREAM NUMBERS		GAS STREAMS		LIQUID & SOLID STREAMS		LIQUID & SOLID STREAMS		LIQUID & SOLID STREAMS	
Temp.	° F	400	70	Temp.	° F	132	400	250	
Pressure	IN WC	+1	0						
Gas Flow	ACFM	20,700	10,300	Flow	GPM			2.3	
Dry Gas	lb/Min	771.0	769	MgO	lb/Min	10.1	10.0		
H ₂ O Vapor	lb/Min	124		MgSO ₃ ·6H ₂ O	lb/Min	181.7			
SO ₂	lb/Min	0.8		MgSO ₄ ·7H ₂ O	lb/Min	10.1			
				MgSO ₃	lb/Min		88.0		
SO ₂ PPM (Dry Basis)				MgSO ₄	lb/Min		4.89		
Fly Ash	lb/Min			Inerts	lb/Min	2.32	2.32		
Mg+S Compounds	lb/Min			Fly Ash	lb/Min	0.273	0.273		
Total Dust	lb/Min			Total Solids	lb/Min	204.5	105.5		
				H ₂ O Liquid	lb/Min	10.7	0		
				Total Flow	lb/Min	215.2	105.5		
				% Solids		95.2	100.0		
				Fuel Oil	lb/Min			18.8	



FIG. 11
MgO REGENERATION SYSTEM

CHEMICAL CONSTRUCTION CORPORATION
1000 PINE AVE. CONTRACTING ENGINEERS

TABLE 6
STREAM PROPERTIES AND COMPOSITION
MgO REGENERATION SYSTEM

STREAM NUMBERS	3	4	5	6	7	8	9	10	11	12	13
	LIQUID & SOLID STREAMS										
Temp											
Pressure											
Flow											
Mg(HSO ₃) ₂											
MgO											
MgSO ₃											
MgSO ₄											
Inerts											
Flv Ash											
Total Solids											
H ₂ O											
Total Flow											
Fuel Oil											
STREAM NUMBERS	1	2	14	GAS STREAMS							
Temp.											
Pressure											
Flow											
Flow											
Total Dry Gas											
H ₂ O Vapor											
Total Wet Gas											
SO ₂											
O ₂											
Dry Gas MW											

is equipped with a vibrating hopper bottom, O-506, and elevated on a structural steel support for direct gravity loading of the returning trucks.

The gas from the calciner, containing SO_2 and products of combustion, as well as a small percentage of excess air, is first partially cleaned of particulates in the cyclone dust collectors P-075. This is a dual cyclone array, designed for a 1 in pressure drop. The collected solids are returned to the calciner with the feed to the unit.

The partially cleaned calciner gas containing 8-10% SO_2 is further cleaned in a venturi scrubber of Chemico's special design, operated at a pressure drop of approximately 25 in of H_2O where it is also adiabatically saturated. Next the gas enters the separator tower section, which is an integral part of the venturi equipment. The lower section of this $4\frac{1}{2}$ ft diameter vessel serves as a cyclonic liquid separator and the upper section, containing eight feet of $3\frac{1}{2}$ in pall rings is irrigated with cooled weak acid to further reduce the temperature of the gas to 100°F in order to maintain the acid plant's water balance. A slip stream of the cooling liquor is stripped of dissolved SO_2 in the weak acid stripping tower P-502, a small (15 in diameter x 14 ft high) packed contactor.

The stripped SO_2 joins the main gas stream and is ducted to the acid plant² in 18 in diameter, FRP pipe.

3.2.3 Acid Plant Modifications

The regeneration of magnesia, described in the previous section, produces an off-gas from the calciner approximately 100 fold richer in SO_2 than the power plant combustion gases treated in the SO_2 Absorption System. The calciner gas is of sufficient strength to be used as a feed for the manufacture of sulfuric acid.

The small, sulfur burning acid plant (Sec. 3.1.2) required some modifications to enable it to accept the calciner gas. Provisions were also made during these modifications allowing the plant to burn sulfur as an alternative source of SO_2 , or to operate on a combined feed from both

combustion of sulfur and gas from the regeneration plant. These modifications are shown in the Process Flow Diagram, Fig. 12.

The principal element replaced in the acid plant was the Main SO₂ Blower, K-901. The original blower handled only air required for the conversion of SO₂ to SO₃ and was not designed to be gas tight (as required when feeding the acid plant with gas containing SO₂), or capable of the required control of suction pressure for operating the regeneration plant. The replacement blower is an axial flow compressor of 5,240 CFM capacity driven by a 200 HP motor. It is capable of a suction pressure of up to 44 in of H₂O for the venturi pressure drop, duct and equipment losses, and calciner draft at the regeneration plant, and a 75 in H₂O discharge pressure for the acid plant. The unit was designed to handle either air or a typical feed gas as shown below:

Acid Plant Feed Gas

SO ₂	6.8%
O ₂	9.4%
N ₂	74.7%
CO ₂	8.1%
CO	0.9%

The blower was equipped with an adjustable recycle control in order to accommodate the variable feed rate of the regeneration plant.

Another important element added to the acid plant was the Cold Heat Exchanger E-901. This piece of equipment supplies the heat to the incoming cold calciner gas equivalent to that available in the gas when burning sulfur in the sulfur furnace. This is necessary to ensure that the gas entering the first mass of the primary converter is hot enough to sustain the reaction. The exchanger, E-901, is a vertical shell and tube unit 3 ft diameter x 9 ft high containing 1700 sq ft of surface. Hot gas exiting the secondary

converter enters the tube side on E-901 and heats the calciner gas passing through the shell side to 540°F.

In the acid plant, calciner gas enters (Stream 1 on Fig.12) and is diluted with sufficient air through the air filter for conversion and passes to the acid plant's drying tower where it is contacted with 93% sulfuric acid to remove the water from the gas. Entrained liquid is removed in F-901A, the Dry Tower. Any SO_2 absorbed by the 93% acid in these towers is stripped in the new 93% Acid Stripping Tower (F-903), a 30 in diameter x 15 ft high ceramic tower containing a 10 ft bed of $1\frac{1}{2}$ in saddles, and returned to the main gas stream. The small amount of additional air is used for trim of the oxygen concentration. The gas is pressurized by the SO_2 blower and enters the Cold Heat Exchanger, passes to the Converter Heat Exchanger E-902 and finally enters the converters H-901 A & B. The heat balance for the conversion step is maintained by using the gas from the second mass of the Primary Converter, H-901A, to heat the gas from the Cold Exchanger, and the gas leaving the fourth mass of the secondary converter to heat the incoming feed.

Next, the stream containing 6.7% SO_3 is contacted with 98% H_2SO_4 in the Absorption Tower F-902 A & B. The gas streams from these towers are first demisted in R-902 A & B, then the remaining SO_2 is removed in the Tail Gas Scrubbing section shown in Fig. 13 to reduce the concentration of SO_2 leaving the plant to allowable levels.

The absorbant used in the Tail Gas Scrubbing section is NaOH solution.

In order to allow a rapid change to sulfur burning, when the plant is operated on 100% calciner gas, the sulfur furnace was equipped for oil firing. The combustion products from this operation are vented to the atmosphere through a short stack which could be bypassed. In normal operation, however, sulfur was burned concurrently because of a low MgSO_3 feed rate. This procedure had the advantage of allowing a rapid change should the calciner gas flow be interrupted. The alternative was possible because of the several dampers which had been incorporated into the ductwork.

NOTE:

* NaOH WATER MAKE UP TO
RECYCLE TANK & EFFLUENT
BLEED FROM RECYCLE PUMP
ON A BATCH OPERATION

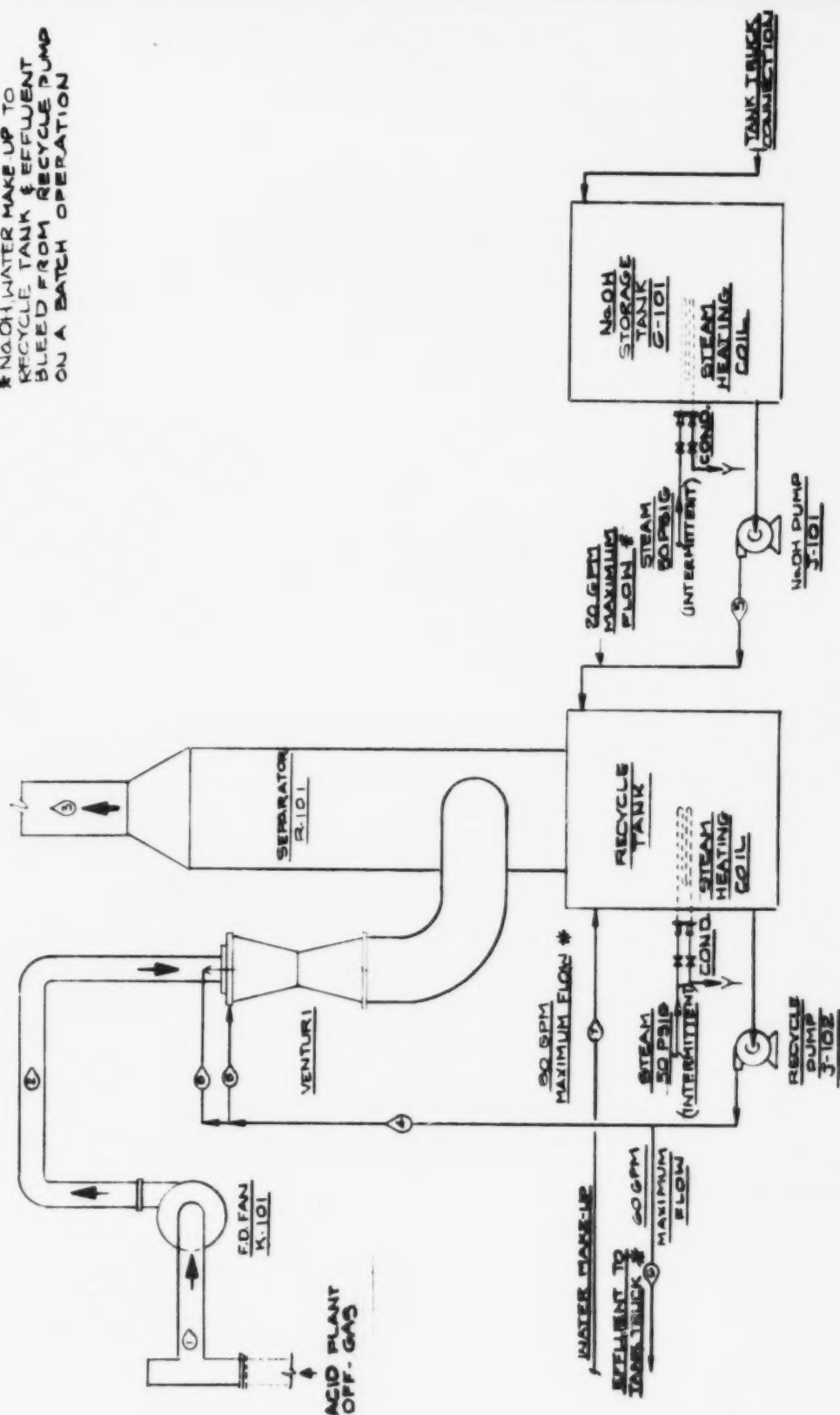


FIG. 13
TAIL GAS SCRUBBING SYSTEM

TABLE 7

47

4.0 DESCRIPTION OF WORK PERFORMED

In order to proceed with the development of the process in the large prototype, the program was organized into a series of tasks as follows:

- a) Construction
- b) Pre Start-Up
- c) Start-Up and Break-In
- d) Planned Operational Tests
- e) Operational (Long Term) Tests

A schedule was established for the completion of these tasks; however, some slippage from this schedule was experienced as outlined in the following sections. A comparison of the actual and predicted schedule showing the dates of initiation and completion of the important tasks is shown in Fig. 14.

4.1 BOSTON EDISON

4.1.1. End of Construction Phase

Labor shortages in some crafts and material delivery delays were the main problems encountered which resulted in delaying the construction schedule so that tie-in to the scrubber could not be made before the end of 1971. The two principal items which had to be completed after the tie-in was made were the precrete work in the ducts and the scrubber lining application. The precrete work was started towards the end of January 1972.

The cold weather at that time of year made it necessary to enclose the absorber vessel in canvas and provide heat in the enclosure so that the FRP liner could be applied at the proper temperatures. Application of the liner was started by the middle of February and was completed by the first week in March.

The check-out of the dryer, centrifuge and air compressor was completed by the middle of February and installation of the mist eliminators in the absorber was finished by the

NEW ENGLAND SO₂ CONTROL PROJECT SCHEDULE DATE

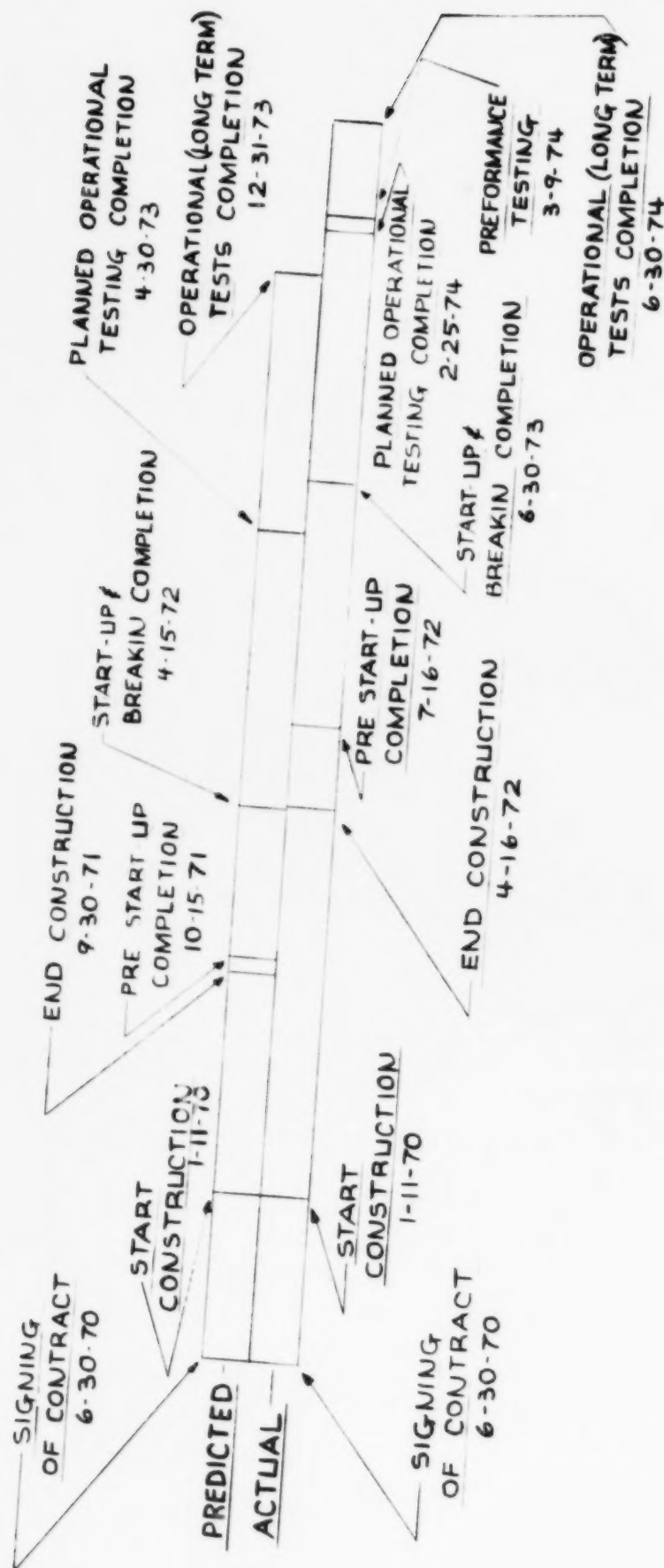


FIG. 14

middle of March.

A mechanical check-out of the dampers prior to the removal of the blanking plates isolating the scrubber showed that different linkage and stronger operators were required before the dampers could be put into service. This work was accomplished during the first three weeks in April. The initial MgO charge was also received during this period. By the end of April 1972 mechanical check-out had been completed ending the construction phase.

4.1.2 Pre Start-Up Period

The trial operational period was started on April 16, 1972 periodically taking gas to the absorber with the boiler on low sulfur fuel. On April 26, the boiler was switched to high sulfur fuel and, for the first time, solid MgSO_3 was removed from the system. During the following few days several new problems were encountered. The solutions to these problems were to consume considerable time and effort during the balance of the year.

While these problems did cause delays in the demonstration of the prototype, it had been shown in the first brief period that the scrubber was capable of performing its primary function, removing sulfur dioxide from the power plant flue gas. SO_2 removal efficiencies of 90% or greater were measured during some of these early runs.

The first and most frustrating of the problems was the change of crystal type and size in the scrubber slurry which made subsequent centrifuging and drying difficult.

Typically, the scrubber would be put on the line when the solids content built to the concentration for initiation of centrifuging and the slurry contained large crystals of MgSO_3 . This, in turn, produced a dry, sandy centrifuge cake. After a short period of continuous operation, usually on the order of 8-12 hours, the centrifuge cake rapidly changed from a sandy to a fluid, creamy consistency. It was found that in the initial operational period of the system, the crystal distribution in the slurry was either larger than 200 mesh or smaller than 325 mesh with little material distributed between these two sizes. (A 200 mesh size was

adopted as the dividing line between describing larger and smaller crystals.)

The crystal size found after the change in centrifuge cake characteristics was generally less than 325 mesh. This same change from a coarse to a fine crystal could take place even though the scrubber was not in operation. If the scrubber was placed on line and then had to be taken off the line before centrifuging, it would be found the following day that most of the crystals in the slurry would be less than 200 mesh.

The change also appeared to be associated with temperature, since the crystals appeared to increase in size if the scrubber slurry were allowed to cool. There was also evidence that the level of magnesium sulfate in the system had some influence on the size of the crystal formed.

Early investigations indicated that the coarse crystals were the hexahydrate form of magnesium sulfite, and the small crystals were the trihydrate form. Some work was done in an effort to find a way to keep the crystal mass in the hexahydrate form, however, the factors that control the crystal type had not been clearly defined.

Operating policy was still to "shut down" when the centrifuge cake consistency changed. All attempts to control the system to produce +200 mesh crystals, by lowering pH, adjusting slurry solids, etc. were unsuccessful. At this point consideration was given to a process change in which bleed stream to the centrifuge would be cooled and then retained in a holding tank till a desired crystal size was attained. An air-slurry cooling tower was designed and installed and a thickener and associated pumps brought to the site to pilot this operation on a five gallon per minute scale. This scheme was never tried, however, principally because the scrubber would have to operate in some continuous mode to provide a feed for the pilot plant and no more than a few hours of operation at a time could be attained. The practical solution to this problem was associated with the solution to a completely different one which arose in the first operation.

When the centrifuge cake was first fed to the dryer it was found that most of the material could not get through the dryer, rather, the dried product was entrained and carried out of the dryer with the off-gas stream. Throughout May, June, and early July of 1972 a series of modifications were made to the dryer design to allow a reduction in dryer gas velocity while still providing a drying capacity. The most significant of these was the removal, in a series of changes, of most of the flights in the dryer drum. In addition, the feed end dam was increased in height to reduce spill back and the top of the feed screw housing in the dryer was cut away to allow cake which was adhering to this housing to fall into the screw and be reconveyed to the drum.

As a result of the dryer modifications, all the flights had been removed from the feed end of the drum, and on some occasions it was noted that the dryer feed would agglomerate in the feed end and pass through the unit in the form of lumps. These lumps ranged from balls about one inch in diameter, to larger agglomerates up to 18 inches in diameter. These large agglomerates caused problems in the material handling equipment after the dryer, and even the smaller pieces could not be handled by the pneumatic unloading system when the magnesium sulfite was shipped to Rumford so that the policy of shut down of the F.G.D. system as soon as troubles developed was continued.

A separate problem which hindered the early runs was a rapid build-up of solid material on the damper blades and frames in the fan and outlet ducting. This build up made the dampers difficult to open when putting the scrubber on the line. Several minor modifications were made in an attempt to overcome this difficulty, but it was finally necessary to replace the pneumatic operators with more powerful ones developing sufficient torque to break the dampers loose from the accumulated material.

During this first period the dryer burner was still another problem source as it was subject to frequent flame-outs and a tendency to coke in the burner block.

All of these difficulties limited the duration of operating periods to less than 24 hours and resulted in frequent

"dumping" of the scrubber slurry as attempts were made to maintain the "sandy" centrifuge cake.

4.1.3 Start-Up and Break-In Period

By early July 1972 it was evident that the crystal type and size produced in the absorption step could not be controlled by any simple changes in the equipment or operating conditions. The technique of allowing the scrubber slurry to cool to form larger crystals had had sporadic success and was not a satisfactory solution. Any significant process changes would have required extensive pilot testing, and no facility for this testing was available.

The intermittent operations of the previous month did indicate that successful operation might be possible if the centrifuge cake could be made to granulate, if there were no adherence of the centrifuge cake to the dryer shell, and if the agglomerates could be handled in the subsequent equipment.

A test was planned in which the dryer temperature profile would be adjusted to give the maximum feed end skin temperature possible, consistent with good operation, to see if the build up problem could be eliminated by the formation of agglomerates.

Feed was to continue to the dryer when the consistency of the cake changed unless there was an indication of heavy build-up or other serious problems. This test run was started on July 18, 1972.

The operation proved to be successful and the system ran for three days. During this time other unrelated problems were encountered causing two brief interruptions. The first was flame-out in the dryer resulting in a 12 hour interruption. A breakdown of the MgSO_3 weigh feeder in the materials handling train caused the second six hour stoppage. During this second stoppage, the flue gas was diverted from the scrubber using the dampers, but all other equipment was kept operating to facilitate return to service of the system. After a temporary chute was installed to bypass the MgSO_3 weigh feeder which had caused the trouble, the unit ran for an additional thirty hours before a tear in the dryer feed

conveyor trough forced a termination of the test run. This breakthrough operation demonstrated that no major changes in equipment or process would be required to continue with the planned operational program. Additional improvements and modifications were required, however, before the system could operate for the long durations necessary to determine availability and commercial applicability.

Corrosion in areas of the duct was also noted during this time. These were temporarily patched while plans were made to protect the parts of the gas flow system which had not originally been protected by ceilcoat or precrete.

These difficulties limited operations to an intermittent basis for several weeks while corrective action was taken.

The scrubber again was put on the line late in August, and operated continuously for five days, except for a brief 6 hour period when the boiler was out of service for minor repairs. During this run, all equipment functioned satisfactorily with the exception of the dryer burner. Although the burner was no longer subject to flame-outs, now not enough fuel could be burned to provide enough heat input to dry the centrifuge cake properly. In order to compensate for this the draft through the dryer was increased, and in turn, resulted in excessive amounts of dust being carried out of the dryer and into the boiler stack. The situation gradually became worse, and on August 31st, it was decided to suspend operations until corrective action could be taken.

During the August run, the scrubber system was shown to be capable of adapting to the changing boiler load which typically was about 150 MW in the daylight hours and 30 MW at night. The scrubbing efficiency observed during this run was also consistently high.

September and part of October were spent in making capacity checks on the dryer burner, velocity checks on dryer gas flow, and entrainment checks on the scrubber itself, and no operations were conducted. System modifications were also completed during this period including installation of a lump breaker for the dryer product, a dust collector for the magnesium sulfite weight totalizer and installation of

a low sulfur fuel supply to the dryer burner as the burner capacity checks in early September had shown that the unit did not burn its rated amount of high sulfur fuel.

This latter problem was attributed to the properties of the station's fuel. Nominally a #6 oil, it contained a relatively large amount of volatile material so that when the oil was heated to the temperature necessary to obtain the proper viscosity for atomization in the dryer burner, the volatile component would vaporize with the subsequent flashing restricting the capacity of the burner. To overcome this limitation, piping was installed to allow the dryer burner to draw upon the station's low sulfur fuel supply. Later, additional work was done on the burner which allowed it to operate at a higher pressure, and thus prevent the flashing of the volatile fraction of the oil to make it capable of operating at rated capacity on either fuel.

The dryer gas velocity checks showed that high dryer draft caused the excessive dust carryover experienced on the run in late August. These tests also showed that even under normal operating conditions the dust carryover was higher than desirable as the dryer was originally designed to process a much coarser material than the fine material which was formed in the prototype system.

The system was returned to operation in mid-October following adjustment and debugging the new equipment which had been installed. A forty-hour run filled the magnesium sulfite storage silo. Magnesium sulfite was hauled to the calciner operation in Rumford and the first 74 tons of recycled magnesium oxide was returned to Boston and added to the magnesium oxide silo. The scrubber was put back on the line on October 21st, and within 12 hours, recycled magnesium oxide was being fed to the scrubber system. At that point, severe plugging occurred in the MgO slurry piping, and the system had to be taken off the line.

It was found that this first recycled magnesium oxide varied considerably in its properties. Much of the material was over calcined (hard burned), and the coarse particles did not slake when the MgO was slurried. After clearing the piping system and installing flush-out connections, for future use the scrubber was again returned to operation, but

plugging of the MgO slurry system continued to be a problem.

Plugging of the MgO slurry system continued after the calciner operating conditions were modified to produce a softer, satisfactory burn material. Indications were that a grinder was required to reduce the particle size of the calcine, so that a slurry could be produced free of large particles and grit. Enough data were obtained during this period to show that the pH of the scrubber slurry could be maintained at the proper level, and that the pH and free MgO level was sufficient to remove 90% of the incoming SO₂.

During the month of November, a scheduled outage of the #6 boiler was taken for maintenance and repair. During the same period, maintenance was planned for the SO₂ abatement system. Principal items of work done were precreting of the fan housings to prevent the corrosion caused by condensation in the duct work. The recycle pumps were inspected and severe erosion-corrosion was noted on the impellers and wear plates. The impellers were replaced from spare parts and orders placed for stainless replacements. All the other pumps were inspected at this time. Additional steam tracing was installed where necessary for freeze protection during the upcoming cold weather. A preliminary attempt to heat the MgO slurry tank was made. A DuPont SO₂ analyzer was added to the system to monitor the inlet and outlet sulfur dioxide concentrations, as the analyzer installed originally proved to be unsatisfactory as it plugged up during brief periods of operation.

An inspection of the scrubber at this time showed no heavy deposits, but there was a light build-up of solids in the vicinity of the tangential nozzles. The scrubber lining was found to be intact and in generally good condition except for some wear on the vertex of the torus where overlapping spray patterns had caused abrasion of the FRP lining.

A serviceable Micro-Pulverizer was located at the acid plant and evaluated. These tests indicated it would produce a ground product suitable for reuse in the system. This unit was a 2D-H model with a 10 HP drive.

By December, the pulverizer had been installed at the discharge of the MgO weigh feeder at Mystic Station and an

attempt was made to return the system to operation using recycled MgO. The run was aborted after a brief operating period when the pulverizer plugged.

This plugging problem was caused by tramp material and clinkers of calcined MgO. Most of the tramp material was uncalcined MgSO_3 which had not been completely unloaded from the trucks prior to loading with MgO.

Vibrating screens were installed to scalp off the tramp material prior to introduction into the pulverizer feeder, but because of limited clearances around the MgO feed system and high maintenance requirements, this was not successful.

During the few short periods of operation in December, heavy build-up was also experienced in the dryer drum. The dryer feed caked on the walls to the extent that a shut down of several days duration was required to clean it.

Also during December, Boston Edison Company asked the local and state authorities for an extension of the time limit for the installation of pollution abatement equipment on their new Mystic #7 unit which was under construction. The appeal was based on the demonstrated progress of the MgO process which had been gained in the operations at Mystic Station since April. The appeal was granted in January 1973.

In the first quarter of 1973, several major modifications were made based on the previous operating experience to improve the "on stream" time of the system. In January, the dryer off-gas was re-routed to the inlet of the scrubber for particulate matter emissions control after numerous other schemes had been evaluated and rejected for control. This selection was based on the conclusion that the 6 inch pressure drop across the F.G.D. systems venturi scrubber was sufficient to control the solids carried over from the cyclones of the dryer. The pulverizer was also moved from Boston to Rumford and installed at the discharge of the magnesium oxide product conveyor.

Over-load of the dryer feed screw which had caused some shut downs was associated with an excess of magnesium oxide in the centrifuge cake. Tests showed that slaking of MgO could be improved by heating the MgO slurry tank. A steam

sparger was installed in the tank and slurry temperatures up to 190°F attained.

Other work undertaken during this period included attempts to remove tramp material recycled to Boston by installing screens at the MgO weigh feeder discharge. MgO proved difficult to screen as it adheres to surfaces and wires, blocking even the coarsest screens tried, ½ inch mesh. A pre-mix tank was substituted to allow the grit to settle while the ground MgO is fed to the slurry tank as overflow. As a precaution, a stand-pipe was installed on the discharge nozzle of the MgO slurry tank allowing agglomerates to be blown down on a regular basis.

The improved operations during this period proved the efficacy of the modifications; however, dryer build-up continued as the most frequent cause of shut down. In April, a final series of changes and additions were made to improve operations. These were: installation of "hammers" on the dryer, a pneumatic conveying system to take the cyclone underflow and dryer spill-back directly to storage, and lengthening of the dryer conveyor in the dryer. A modification to the pre-mix tank was made to prevent blockages of the down comers and new design damper operators were installed in an attempt to overcome the old sticking damper problem which had delayed numerous start-ups throughout the program. In a preliminary run at the end of April most of the old problems appeared to be corrected, and it was considered possible to enter into the next phase of the test and development program to provide data which would lead to improved operations and optimization of the system.

4.1.4 Planned Operational Testing

Initial operations in May 1973 indicated a substantial improvement in the process reliability. Slaking of the MgO slurry at a temperature of 180°F reduced the consumption of MgO required for pH control and proper SO₂ removal. Analysis of the centrifuge product indicated a substantial reduction in the amount of free MgO indicating a greater utilization of the recycled alkali in the absorption step.

A labor problem at the station in May prevented further operation of the system during that month. Upon resumption

of work in June, the dust handling system was completed and the system was started up.

During the month of June nine interruptions occurred. Six of these outages were caused by boiler related problems but the other three were failures of the F.G.D. System. These three were: first, a stalled dryer feed conveyor caused by neglect to clean the dryer feed screw before the system was returned to operation; second, a dryer upset caused by a large agglomerate jamming the dryer product screw; and finally, a shutdown because of high level in the dryer product silo. The latter resulted from insufficient equipment to transport $MgSO_3$ at the rate it was being produced.

In all, during June, 376 hours of operation were logged and scrubber availability to the boiler increased to 68%.

Operations of the system continued into July. The main difficulty to operations being the constant attention necessary to prevent the MgO pre-mix tank from plugging. On the 4th of July, the #6 boiler developed an economizer tube leak and was shut down. During this outage leaks in the recycle piping and valves were patched, and a revised pre-mix tank was substituted. A manual valve was also substituted for FCV-5 controlling the flow to the centrifuge as the pinch valve, which had been part of the original design, proved to be unsuitable. The system was returned to service on the 6th but deposits on the dryer feed screw and in MgO pre-mix tank which had to be removed on a regular basis by the operators and leaks which continued to appear in the recycle piping caused operating difficulty. In addition, a blockage (later found to be a plastic bottle) occurred in the centrifuge feed line restricting flow. A boiler tube failure on the 14th terminated this run.

A stack inspection was performed at this time, and it was found that the upper 10 ft of the inner stack was damaged (this damage was unrelated to the F.G.D. system). The boiler was returned to service on the 15th, and the F.G.D. system ran till the MgO supply was exhausted on July 19th. When sufficient MgO was received, the plant was returned to operation and continued in service through the 27th, with two boiler tube failures and some absorber system related

problems causing a number of short interruptions during that period. A scheduled boiler outage was taken on July 27th and maintenance on the boiler and the absorption system occupied the rest of July and most of August.

No. 6 boiler was back on the line on August 28th, and the absorption system on the 30th; however, difficulty was again encountered with sticking booster fan dampers which was not corrected till September 6th. A series of attempts to restart the system were aborted by:

- 1) A leaking centrifuge oil cooler
- 2) Dryer feed screw binding
- 3) MgO feed problems

On September 15th the system was returned to operation and during the first three day period several minor problems were corrected with the F.G.D. system in service switching from high to low sulfur oil. Smooth operations were obtained from the 18th through 21st but again a low MgO supply forced a shut-down after that time.

The inventory was replenished and the system restarted on the 24th, but after a short period it had to be shut down because of a slurry leak which developed at the centrifuge feed port. The cause was fractured centrifuge feed pipe, and four days were taken to correct this problem as the centrifuge was also dismantled for an inspection.

Operations continued intermittently during the first half of the month of October, with only 78 hours of system operation achieved by the 15th. The interruptions were a series of breakdowns of process equipment interspersed with a series of boiler related failures. The F.G.D. problems were: debugging the new cyclone underflow conveying system and in the MgO pre-mix system.

A 40 hour run started on the 16th was shut down because of a boiler tube failure. Repairs to the boiler were made but the units' return to operational capacity was limited by a failure of the refractory in the dryer burner block which prevented firing it at its full rate. The system was

switched temporarily to low sulfur fuel to control solids level but another boiler tube failure on the 18th terminated the run, and the system was idle til the 20th. From the 20th until the end of the month, the system operated for 106 hours with one interruption, a 17 hour outage caused by depleting the supply of MgO. After transferring a fresh supply of MgO the system ran for an additional 87.5 hours, but was forced to shut down after the MgSO_3 silo at Mystic filled to capacity with resultant damage to the materials handling equipment.

While the MgSO_3 was being transferred, the dryer feed screw gear box and the product bucket elevator were repaired, and operations resumed on November 9 and continued through the 15th with only a 4.5 hour interruption for lack of MgO. From the 16th through the end of the month the unit was down, as the MgO supply had been exhausted, and as a result of a shortage of fuel oil for the calciner. Over-all utilization for the month was 24% based on available hours; utilization for the week ending November 16th was 84%.

During the short operating period in November a stack testing program was conducted and a second series of scrubber emissions tests was run. A separate particulate matter emissions test was also conducted by the Environmental Protection Agency.

Operations started again on December 7th after the fuel oil situation had been resolved, and during the next two weeks continued sporadically with numerous interruptions caused by malfunctions of the cyclone overflow conveying system and leaks in the main recycle pumps.

The pump maintenance could not be accomplished because the plug valves to isolate them were severely eroded, requiring that the system be drained to work on it. A planned outage of the absorber system was taken to replace the pumps and plug valves and to patch several other leaks which had developed in the top piping. This limited plant operations to 86 hours during the month of December. The system was returned to service on January 10, 1974 but again a series of mechanical problems, including an outage of the boiler, caused intermittent operation of the absorber and numerous switches between high and low sulfur fuel oil in the boiler.

By January 25th, most of the new problems were corrected and testing was resumed, but after 30 hours a boiler tube failure required a two day repair outage. When the unit was started up again difficulty was experienced in controlling the recycle solids concentration in what appeared to be a reduction in centrifuge separational efficiency. Operations were terminated to investigate this, and the centrifuge was dismantled for inspection and repair.

During January, the system was operated an additional 147 hours to give a total for December and January of 233 hours. During this period inventory control was initiated and the inventory showed a loss of 80 tons of MgO in the two months operations.

The absorber system was not returned to service until the 19th of February, 1974 while the centrifuge was being repaired. During this same outage several maintenance items were completed including the installation of a heavy duty weigh belt on the MgO weigh feeder, venting the dust collector in the $MgSO_3$ silo, replacement of couplings on the recycle pumps, and the installation of several sample nozzles for the stack testing to be conducted later in the month.

The system was started up again but ran only two days before depleting the supply of MgO . The coordination of shipments of material between the two plants was made the responsibility of the chief Chemico operator to correct this recurrent problem. Because of the decision to use only regenerated alkali while conducting the performance tests there were no further operations until the 25th in order to conserve the MgO inventory. During this wait the by-pass dampers were calibrated and tested to prepare for a new mode of operation in which a part of the flue gas would be bypassed so that the system could be operated at its design gas flow. Previous testing had established that the system was handling as much as 650,000 ACFM when the boiler was being operated at full load (as compared to the design 440,000 ACFM) because of leakage into the ducts ahead of the boiler ID Fan (Table 8).

Also, for the tests, the dryer off-gas which had been routed to the absorber system in a corrective modification, was reverted to the stack in order to eliminate this

TABLE 8

FLUE GAS DESULFURIZATION - MYSTIC #6

ABSORBER GAS FLOW

Date	Boiler Load (MW)	6-1 Duct		6-2 Duct		Total
		Total Air (%)	Gas Flow (ACFM)	Total Air (%)	Gas Flow (ACFM)	6-14 6-2 (ACFM)
11-25-70 ⁽¹⁾	142	153		153		
11-27-70 ⁽¹⁾	142	163		160		
10-11-73 ⁽²⁾	150					573,000
10-11-73 ⁽²⁾	149					523,807
10-14-73 ⁽²⁾	149					645,000
3-5-74 ⁽³⁾	151		335,411		322,796	658,207
DESIGN GAS FLOW						440,000

(1) Boston Edison Company Communications

(2) Custom Stack Analysis Co. Report

(3) York Research Corporation Report
Y-8419, 4/11/74

additional solids emission load on the scrubber, as it had not been part of the original design.

The system was started on February 25th for the first performance tests of the program, but a boiler tube leak on March 1st forced a shutdown.

Also during this period, additional tests were conducted over two days using humidification sprays to determine if pre-quenching could influence the hydrate formed, and whether there would be an improvement in the outlet dust loading. The results obtained from the humidification test indicated that there was no effect from their use.

Repairs to the boiler were completed on March 5th. The F.G.D. system was put in operation, but again a boiler tube failure forced termination the following day. The F.G.D. system was restarted immediately after boiler repairs were completed and ran satisfactorily for two days before a third boiler tube failure forced an outage; however, the performance testing was completed.

4.1.5 Operational Testing

Operations during the test period indicated that reduction of gas flows nearer to design in the system, coupled with the extensive repairs and numerous improvements and modifications, had resulted in a more reliable and controllable system. With the substantial experience and operating information gained in the preceeding two years, it was decided to start a period of continuous operations at a fixed set of conditions. Preparatory to starting this new phase the blanking plate, which had been removed from the dryer gas stack breaching for the test work, was reinstalled so that the scrubber controlled this particulate discharge source.

The F.G.D. system was returned to operation on March 12th and ran smoothly. On the 15th another boiler tube failure occurred, repairs were made and operations resumed on the 18th but were stopped on the 19th by another failure. Boiler repairs were completed by the 21st, and the F.G.D. system ran through the 26th when again a boiler failure forced an outage. The system came on as soon as boiler repairs were completed on the 28th, but was forced out because of a

boiler tube leak the following day.

During this period, there were also four malfunctions of SO₂ abatement system equipment. The first, on the 18th, was a broken chain on the cyclone underflow star valve. These repairs took three hours, and during this time the system was kept on the line on low sulfur fuel. The second was a blockage of the dryer screw conveyor on the 22nd (low dryer temperature allowed wet material to get into the screw conveyor). This was corrected in 4½ hours, again, without taking the system off the line. The third incident did force the unit off the line and was caused by a failure of a small agitator in the MgO pre-mix tank. A replacement was on hand but was found to be defective, and an outage of 11 hours had to be taken to repair the agitator. The fourth interruption was a four hour outage to replace a broken chain on the MgO weigh feeder drive.

When the F.G.D. system was being restarted on the 30th a bearing failure was noted in the MgSO₃ elevator, and no operations were conducted for the first four days of April, while waiting for repair parts. The system was started on the evening of the 4th and ran continuously through the 11th. A carbon deposit in the dryer burner block caused a hot spot and the system had to come down for one day for repairs, but was again in operation on the 13th. It ran continuously through the 19th, when a boiler tube failure forced it off line. Boiler related failures on the 22nd, 23rd, 24th, 26th, and 29th of April resulted in interrupted operations; however, they also further demonstrated the capability of the F.G.D. system to cycle with the boiler. Despite the aforementioned problems April operations were smoother, and one hundred percent availability was achieved for the two week period from the 6th through the 19th. In all, during April, the absorber system operated for 471 hours out of 585 hours available (because of the numerous boiler failures) for an 81% utilization.

One hundred percent availability of the system was again achieved during the first two weeks of May. Then the system was forced down on the 14th when the MgO supply was exhausted because of acid plant outage. The acid plant outage necessitated shut down of the regeneration section. MgO production was resumed in late May after the acid plant

had been repaired.

Before starting again three additional days were taken to clear the system of MgO and $MgSO_3$ prior to starting an MgO Loss Identification and Inventory Control Program. During the month of May, 1974, boiler tube failures on six occasions were the major cause of program interruptions. The boiler and F.G.D. system were operational from the 4th through the 5th, the 11th through the 14th, and from the 28th through the 30th, a total of 280 hours out of 488 available.

One hundred percent availability of the system was again achieved during the first two weeks of June. The MgO Loss Identification Program was concluded on June 18, 1974 (the MgO feed bin was deliberately run empty to finish this test). SO_2 addition runs were made on June 13th and June 14th, with the injection of four tons of liquid SO_2 into the system to increase inlet concentration to its design value. But overall availability for the month was still limited because of seven boiler tube failures. Two hundred eighty-eight hours of F.G.D. system operation were achieved in 359 hours of boiler operation for an 80% availability.

The program contract termination date was June 30th, 1974 but operations were actually concluded on the 26th when the dryer feed conveyor failed.

4.2 REGENERATION - RECOVERY OPERATIONS (ESSEX CHEMICAL PLANT)

4.2.1 End of Construction Phase

The plant construction had been completed on December 21, 1971; however, operations could not be initiated as the magnesium sulfite needed for feed was the product of the yet to be completed SO_2 abatement plant. In the interim the new main blower was commissioned for acid plant operations in January, and instruction of operators and the first firing of the calciner to "cure" the refractory brick work was done in March.

During this preliminary work the first operating problem uncovered was a low draft at the firing hood caused by

excessive leakage of air through the seals and air intakes of the calciner. This was a potential process problem, as the calciner had to operate with a neutral or reducing atmosphere in order to reduce MgSO_4 which was produced in the scrubbing step. Considerable work was expended in tightening up seals and reducing the air intake leakage. (This did provide some improvement; however, when feed was obtained for processing excess oxygen content in the calciner atmosphere still remained as a problem).

Another problem which was uncovered in this period resulted when firing oil in the cold calciner on start-ups. Hydrocarbon vapors succeeded in passing through the scrubbing equipment installed for gas clean-up of particulate matter and entered the acid plant where the hydrocarbon caused contamination and blackening of the product sulfuric acid. A 1500 CFM fan was obtained, ducted to the calciner and a stub stack discharge erected in order to provide a separate venting system for the calciner on start-up. (This vent is not used when MgSO_3 is decomposing in the calciner).

While waiting to receive dryer product from Boston for actual start up, a high noise level condition from the main blower air intake was also corrected by relocating the intake and erecting a sound baffle around the blower itself.

4.2.2 Pre Start-Up Period

The first dryer product was transported from Boston on June 20, 1972. The necessary coke had been obtained prior to this time and was stored in the coke silo.

Pre start-up was limited to testing the conveying system with the material on hand. Some work was undertaken in matching the elevator capacities as the bulk density and granulation of the material produced at Boston was substantially different from that for which the equipment had been designed based on the original pilot plant work.

The presence of lumps in the feed material caused difficulty in material handling at the regeneration plant in both the pneumatic conveying system and the weigh feeder. (The solution to this problem involved the determination of proper operating conditions for the dryer and was not

implemented til later in the program).

4.2.3 Start-Up and Shake-Down Period

Start up of the system was not initiated until sufficient dryer product was in inventory in insure five days of continuous operation. Material from the Flue Gas Desulfurization system was first fed to the calciner on August 3, 1972. Problems of low draft in the unit and high oxygen concentration in the kiln atmosphere were experienced immediately.

Natural draft occurs in the calciner because of its length and pitch. This draft resulted in high seal leakage at the small gas flows required for proper kiln operation. This caused "puffing" at the feed hood and excessive oxygen content in the off gas. The new corrections for leakage included removing and machining the firing hood seal to provide minimum clearance on the hot shell. The draft doors were sealed, all openings closed and the product discharge ports closed by 50%. This work was done by early September and resulted in a lessening but not elimination of the problem.

During this same period operating policies were developed to overcome the problem of contamination of the product acid by hydrocarbon vapors from the regeneration section. Principally this was accomplished by shunting the combustion gases to the vent stack after the mid kiln temperature fell below 1000°F.

Another serious problem was caused by dusting in the calciner which obscured the flame from the fire control monitors and caused frequent shut down of the kiln on a false "flame failure" signal. Several approaches were tried to overcome the numerous "flame outs" which occurred because of this. These included installation of a second flame scanner for parallel control, and air purging the sight tube on the main scanner, and adding magnifying lenses to it. These improvements did not eliminate the problem as the long nose burner used extends deeply into the kiln and the high level of dust still caused shut down.

In reviewing the problem it was found that normal

industrial practice for operation of dusty kilns was elimination of flame scanning equipment and substitution of direct operator observation and control. Work was initiated at this time to obtain the necessary authorization to operate the calciner this way.

By late September improvement in draft control was accomplished and product of low MgSO_4 content was produced; however, the product MgO was still hard burned. It was found that the MgO slaking method which had been proposed to analyze the product was unsatisfactory, and a decision to enlarge the scope of the quality control laboratory at Rumford was made to develop the necessary new analytical methods for the operation.

During the month of October the calciner was operated for 179 hours. No coke was added during these runs but the MgSO_4 content of the product was held at a low level by increasing the calciner temperature. When this level fell below 3-4%, however, a drop in the MgO activity was noted, the result of overburning of the MgO at high kiln temperature.

The first shipments of regenerated magnesia produced in these operations, was made to Boston in November. Problems in feeding the MgO were immediately encountered there (as described in the previous section). A factor in the problem of using the regenerated, recycled MgO was a large percentage of grit and coarse particles contained in it.

A micro pulverizer was located and first installed on the system at the Mystic Station to control the problems that resulted from the coarseness of the calciner product. This location was found to be unsatisfactory primarily because of space and equipment lay-out limitations.

The annual shutdown of the Mystic 6 boiler taken in early November, coupled with the infrequent operations in December, as solutions were sought to improve the activity of the recycled MgO , resulted in a lack of feed for the regeneration plant. Processing was not resumed until January 13, 1973, after the initial trials.

During this two month outage the pulverizer was removed

from the Boston Edison plant and re-installed at the regeneration facility. It was placed at the discharge of the calciner product screw conveyor after first removing the MgO weigh belt. (The weigh belt had been previously found to be very difficult to keep in operation and its removal did not affect the project.) In addition a magnetic separator and a vibratory screen were installed at the feed hopper of the pulverizer to protect the unit from tramp materials. (This pulverizer, which was available on short notice, was used throughout the project despite the severe service it was required to perform. Its use has enabled gathering information on size distribution in order to specify grinding equipment in the future.)

After restarting the regeneration plant in mid January the modifications and improvements resulted in longer operating periods but a new phenomenon was observed, the occurrence of "slides" in the calciner. These slides were evidenced by a sudden surge of material at the discharge of the kiln which stalled the material handling equipment and the pulverizer. This phenomenon was partially controllable if the feed rate to the kiln was limited to 60-80 lbs/min., (substantially less than 106 lbs/min design). Attempts to eliminate the "slides" were limited to increasing the rotational speed of the calciner in order to reduce the bed depth, and control of the feed rate to reduce the throughput.

Neither of these has been completely successful, and increasing evidence indicates that the dryness and size distribution of the dryer product are also important.

Operating at a 60-70 lb/min feed rate and a 1.56 RPM kiln speed reduced the slide frequency from 30 per shift to 1 per shift. However, with each slide heavy dusting still occurred in the calciner causing a flame-out on the false signal previously mentioned.

After discussion with the fire underwriters, permission was obtained to bypass the flame scanner if an operator was stationed on the firing platform to tend the unit. The elimination of the frequent interruptions in operation resulting from this change to manual control resulted in a great improvement in the quality of the calciner product that could be obtained.

Implementation of the quality control tests for SO_2 efficiency of the regenerated MgO and operator control based on the product bulk density measurements resulted in improvements in both quality and uniformity of the recycled magnesia.

Other changes were made during the first months in 1973 to eliminate recurring causes of operating problems. These were 1) the redesign and installation of a new firing end friction seal in order to minimize air infiltration at this point 2) rebuilding the gas duct at the calciner exit in order to provide a better transition to reduce pressure drop in the system, 3) overhaul of the MgO elevator, and 4) an air intake outside the building provided for the calciner's forced draft fan. All this work was finished by the end of April, 1973.

4.2.4 Planned Operational Testing

Operations were resumed early in May and proceeded smoothly for a four day period. Coke was added at several rates during this period with good results. During this run 120 tons of feed were processed. The calciner product MgSO_4 content averaged 1-3%; SO_2 utilization factors between 50 and 65 were measured and bulk density of 25-30 lb/ft^3 were observed, all indicative of high quality magnesia. These operations raised questions on the role carbon played in the process. There was indication that it smoothed operation because of the different temperature profile obtained with the addition of coke which can act as a fuel in the feed stock.

Before this question could be investigated a strike at Boston Edison cut off the feed supply, and operations were again interrupted for a time. The system was not restarted until early June, and at this time it was decided to reprocess the dryer product without the addition of coke. During the June operations the calciner feed rate averaged 36 tons per day, and 12 tons per day of product were produced and recycled to the absorption system.

While numerous material problems still remain to be solved, it was apparent that the calciner system could

regenerate the dryer product from Boston satisfactorily. Operation of the regeneration system during July 1973 was almost continuous; 125 hours the first week, 164 hours the next week, and a total of 65% utilization during the month with the longest single outage being 24 hours taken to shorten the chain in the MgO bucket elevator. The dusty nature of the feed from Boston did cause numerous brief problems, literally hundreds of floods of the $MgSO_3$ weigh feeders, recycling in the $MgSO_3$ conveyor, etc. In addition the pulverizer motor was found to be too small to handle high flows and stalled out when slides occurred in the calciner. Another new problem that became evident with longer operations was that the O_2 concentration in the calciner could fall too low as equilibrium was attained. (This was an illustration of the efficiency of the improved friction seals). As a result, on several occasions elemental sulfur formed in the calciner which in turn plugged the venturi scrubber.

An acid plant shut down which had been scheduled for the 28th of July was taken and during this time additional improvements were made at the regeneration facility. A 20 HP drive was obtained and installed in place of the 10 HP drive originally furnished on the pulverizer. A variable speed drive was installed on the calciner in the hope of controlling slides through speed variation, and the $MgSO_3$ elevator was examined and plans made to convert it to a continuous rather than a centrifugal unit.

The acid plant was restarted on August 27th and the regeneration plant on the 30th. Problems resulting from the dusty feed noted earlier limited feed rates to approximately 50 lb/min. It was thought that these problems were caused by a segregation of feed in the Boston silo caused by the introduction of the cyclone underflow (fine dust) and more granular dryer product at diametrically opposite points in the silo. During the July-August outage this had been corrected by rearranging the dryer product discharge back to the center of the silo. A program of gradually increasing the feed rate was undertaken, and a 75 lb/min rate achieved by the end of September. Since changes in feed rate resulted in problems in control of calciner atmosphere, reducing conditions were encountered and sulfur formation caused blockage in the venturi scrubber

on two occasions. The oxygen analyzer probe and sampling system were overhauled to eliminate leaks and to give better control.

A period of low pH operations at Boston resulted in a feed of high iron content (4-5% Fe_2O_3), and processing the resulting calciner product resulted in rapid wear in the micropulverizer, but did not stop the processing. Operations were conducted when feed was available with the only interruption an acid plant leak which terminated a four day run (September 14 through 18). A planned shut down was taken on the 26th to coincide with the centrifuge repairs at Boston.

Operations at this plant continued to improve as a result of the better mixing of dryer product from the scrubber operation. A feed rate of 80 lbs per minute was achieved in October, with 60% operation of the regeneration system during the first week and 69% operation during the third week, with most interruptions caused by a shortage of feed material from Boston.

During the week of October 26th, the unit was shut down for additional improvements. A new weigh feeder, live bin bottom, and tapered flight in the calciner product screw conveyor were installed and these improvements further assisted in smoothing the operations so that during the last week of the month operation at an 84% utilization level was maintained.

Operations continued into November, with only one major difficulty, low air pressure to the feeder controller when the instrument air pressure dropped below 45 psig. To correct this a new compressor, Sullair Series 10, was ordered with delivery of the unit scheduled for December.

A bearing failure on the head shaft of the MgSO_3 elevator occurred on November 7th, which shut down the plant. The plant was not restarted after repairs were completed because the availability of both MgSO_3 from Boston and No.4 fuel oil from Essex Chemical could not be assured. In all, a total 152 hours of operation were logged during the month of November.

The fuel supply question was resolved and calcination of magnesium sulfite from Boston started again in early December. During the first and second week of December, the system was operated for 196 hours at better than 60% availability, and 140 tons of regenerated magnesium oxide were produced. Some mechanical difficulty was encountered when bolts loosened in the bucket elevator and a flood at the weigh feeder caused a two day outage during the second week. Operations were briefly continued during the third week and an additional 21 tons of magnesia produced prior to shutting down the system while the Boston unit was being repaired. During the first three week period, approximately 430 tons of magnesium sulfite was processed through the kiln. Sulfur formation in the calciner was experienced once during that period and again attributed to strong reducing conditions in the calciner because of a low O_2 concentration. Plans were made to further redesign and improve the oxygen analyzer sampling system in order to provide a better continuous indication of off-gas composition to control the unit.

Magnesium sulfite was processed through the calcining system during the last two weeks of the month of January, 1974, 72 tons of MgO were regenerated during 115 hours of operation. (Plans to start the system earlier had to be postponed when a defective control valve was found in the main SO_2 blower recycle loop. This was a reoccurrence of a previous failure of the valve seat in the valve. A new seat was obtained and installed.)

During the latter part of the month of January, the new tail gas scrubber system was tied into the plant during an acid plant outage. After the acid plant was restarted, calcining resumed on the 4th of February, but on the following day the system was forced down by a trip of the acid plant blower. During this brief period of operation, the acid plant reported that some of the acid produced was cloudy, an indication of the presence of sulfur in the calciner gas. The shut down period was extended in order to install the new oxygen analyzer sample system.

The bucket elevator was changed from a centrifugal discharge type to a continuous type during the following week. In addition, the tail shaft of the $MgSO_3$ screw conveyor was extended and equipped with a second bearing in order to

improve its service life.

Operations were not resumed until the 26th, as there had been no operations at Boston to produce feed in the previous weeks. When the system was restarted, problems were encountered in the materials handling equipment, principally flooding and recycling of materials in the bucket elevator. This recycling was attributed to a dusty feed being received from Boston.

The interrupted operations resulted in only 100 hours of operation for the month of February, and the production of 80 tons of regenerated alkali.

The calciner continued to operate through the beginning of month of March, but the dusty feed continued to cause materials handling problems. Finally, a bearing failed on the $MgSO_3$ conveyor, and the system was shut down until the 7th. When the system was restarted, a slide caused an overload of the MgO conveyor requiring additional time for maintenance.

A shortage of feed further limited operations, and the plant was not restarted until the 13th of March.

Operations continued through the 15th, when the run was terminated again because of a bearing failure on the $MgSO_3$ conveyor. The low feed inventory was replenished during this time, and the system restarted on the 18th. At this time it was noted that draft control in the calciner had become difficult. The cause of low draft and inability to meet acid plant air requirements were traced to a build-up of dust in the 18 inch duct from the exit of the calciner cyclone to the venturi scrubber. An inspection of this line showed the duct to be almost completely plugged.

The build-up of dust in the duct was an accumulation over approximately 1 1/2 years. This duct had been inspected and cleaned at the earlier time of a two to four inch accumulation. Cleanouts are now scheduled on acid plant turnaround. Additional consideration was given to blanking off one of the cyclones on the calciner in order to increase dust removal efficiency; however, there is a serious problem with draft control, and it is felt that blanking the

cyclone could cause the situation to worsen. (This latter problem results from a higher delta P (35") than expected across the acid plant's drying and dry towers, which are presently packed with 3 inch partition rings.) Regeneration operation resumed on the 24th and continued through the end of the month with a series of interruptions from both acid plant leaks and new problems arising with the renovated magnesium sulfite bucket elevator. Despite the sporadic outages of the regeneration facility, enough MgO was produced so that the SO_2 abatement plant had sufficient inventory to continue operations all during the month. The tail gas scrubber was started up on the 25th, and measurements showed that satisfactory SO_2 removal could be attained in the unit to reduce the acid plant emissions to acceptable levels.

Repairs were made to the $MgSO_3$ elevator, and, except for a few brief interruptions caused by acid plant problems in the early part of April, the system ran until inventory was exhausted. This was replenished over two days, and regeneration was resumed on the 7th of April, continuing through the 12th, when another failure of the tail shaft of the bucket elevator occurred.

The shaft was replaced with a heavier one, and no further breakage was experienced. The previous five day operation had again reduced feed inventory, and this was built-up over the next two days.

4.2.5 Operational Testing

Operations were resumed in mid-April for a seven day period, only stopping after depleting the feed inventory. The plant was down from the 21st through the 27th awaiting a supply of feed. During this period, a leaking emergency water spray in the venturi scrubber which had caused plug-gage of the upstream duct was repaired.

Shortly after starting up again on the 28th, it became apparent that some of the refractory brick in the calciner had loosened. However, $MgSO_3$ regeneration continued through the 3rd of May when the plant was shut down when one of the bricks jammed the product screw conveyor. The problem was identified as two rings of brick which had loosened near the

feed end of the calciner. Spare refractory bricks were on hand so the repair were accomplished quickly, and the system was returned to operation from the 7th through the 14th. At this time repair in the acid plant necessitated a shut down while the waste heat boiler was overhauled and regeneration did not start again until the 24th. This outage did result in a shortage of regenerated MgO for Boston, with operations limited to 152 hours out of an available 280 hours.

Again in June, the final month of the program, interrupted operations at Boston eventually resulted in a shortage of feed for calcination. Thus, the regeneration plant operated five days in the first week of June, and another five days the second week with the interim periods shut down for lack of feed. This same shortage had prevented attempts to achieve design capacity of the calcining facility.

Feed was accumulated during the third week of the month to initiate some rate and capacity checks, but the results obtained were inconclusive. Operations were ended with the program termination at Boston; however, the same facility will be used in a continued program with a coal fired power plant.

In the period from March 8th through June 14th, 716 tons of MgO were regenerated in 935 hours of operation. This can be contrasted with 419 tons of MgO regenerated during 588 hours in the previous four months period.

4.3 SUMMARY OF SYSTEM MODIFICATIONS

During the course of the project numerous modifications were made to both plants. These ranged from major changes such as rerouting the dryer duct to the scrubber instead of the stack, to minor ones such as increasing the size of the calciner bucket elevator tail shaft by $1/8"$. While no major process changes were made or major new equipment required, all of the many changes and modifications contributed to improving the operability of the plants in this first prototype installation.

The purpose of modifications fell in three categories: first to allow the integrated plants to operate continuously; second, to increase the reliability and raise the

capacities nearer design values; and third, to achieve the desired removal efficiencies and demonstrate the regeneration capability of magnesia. In the first category numerous problems at both sites still had to be corrected during the start up period. Sound levels from the acid plant main blower had to be reduced to an acceptable level, pneumatic operators on the ID booster fan dampers at Boston needed to be changed to a size capable of opening the dampers, and capacity matching of the material handling equipment was required.

1. Other modifications required for operation and accomplished in the first phases of the program during 1972 were:

A) Removal of dryer lifter flights in the first and last third of the drum and removal of the lifter lips in the mid-section of the drum, required because the centrifuge cake produced in operation was a much smaller crystal size than that formed in the pilot plant operation. Other dryer modifications included increasing the height of the rear (feed end) dam.

B) The dryer product that was obtained had large agglomerates and was also very dusty. In order to correct this problem, a "finger" crusher was installed at the dryer exit to reduce large agglomerates to 2" maximum. The dust problem took some time to bring under control, and the methods are described in a later section.

C) Corrosion of the fan casings at the 6-1, 6-2 booster fans was corrected by installing a precrete lining in the lower half of the case. The problem was caused by the condensation of vapors in the flue gas in the ductwork when the absorption system was idle. The ducts themselves had been designed and installed with a liner, but the fans, identical to the Mystic 6 ID fans, had not. Installation of the lining corrected this problem.

D) The seals on the calciner were not adequate to prevent in-leakage of air and, thus, a reducing atmosphere could not be attained. The firing end

was modified, all necessary openings closed, 1/2 of the tube cooler air intakes blanked off, and the seals remachined to provide the minimum clearance. This work did reduce air infiltration and MgO was regenerated for reuse in the absorption step (further work was done on improving the firing end seal later in the program).

E) The dusty nature of the material in the calciner created a problem, as the dust continuously obscured the flame, tripping the flame scanners on a false "flame out" signal. Numerous minor modifications were tried to resolve the problem such as:

- 1) Changing optics on the scanners.
- 2) Adding a second scanner.
- 3) Installation of an air blown sight tube on the scanner.

None of these provided a permanent solution.

F) Calcined magnesia leaving the kiln contained a significant amount of grit, which would not slake when it was recycled to the absorption system. This grit also caused pluggage of the MgO slurry lines. A small pulverizer was obtained for test purposes in the prototype. Initially installed at the Boston facility it was demonstrated to be capable of producing a usable grind.

G) The ground regenerated MgO exhibited a low reactivity, causing difficulty with pH control and SO₂ removal. This was corrected by heating the MgO slurry tank to 180°F to activate the magnesia. Heating was accomplished with a direct stream sparge to the tank controlled by an appropriate temperature controller.

2. In the second category several modifications were accomplished in 1973:

A) Re-routing the dryer off gas to the absorber to control particulate matter emissions. The dryer

had originally been equipped only with cyclones for dust control of the gas passing to the stack. It had been predicted earlier that these would not be suitable, however, as there was no experience with such a system, the cyclone arrangement was investigated before arriving at the final design. After testing of particulate matter had revealed a 10 gr./SCFD inlet and 1 gr./SCFD outlet from the cyclone, it was decided to use the absorber for the final dust control. This was accomplished by installing a direct connection to the 6-1 ID Booster Fan inlet or outlet, with a damper control to select the injection point for absorber in-service or out-of-service application.

B) The pulverizer was relocated to the regeneration facility and installed at the discharge of the MgO screw conveyor (O-503). Also installed at the same time were a vibrating screen and a magnetic separator to remove any tramp material from the calcined MgO before it entered the pulverizer.

C) A hammer mill was installed at the truck loading station at Mystic to reduce oversize lumps scalped off at the discharge of the belt conveyor (O-408). MgSO_3 out-loaded to trucks from this belt contained a significant percentage of $+3/4"$ size lumps (10%) that had, to this point, been discarded. A chute was installed from the scalping screen to the newly installed hammer mill. The pulverized MgSO_3 discharging from the mill was then returned to the belt by means of a conveyor installed at the same time.

D) External hammers were added to the feed section of the dryer and the feed screw extended into the dryer to eliminate adherence of material to the shell in this area.

E) A friction seal to replace the original labyrinth seal was designed and installed at the firing hood of the calciner to further reduce air leakage at this point. This, coupled with the previous

fixes, allowed the attainment of a reducing atmosphere in the calciner. Additional control of kiln operation was provided by the installation of a variable speed drive for the range 0.7 to 2 R.P.M.

F) A pneumatic dust conveying system to handle the cyclone underflow and dryer spill-back was designed and installed. This finally eliminated a problem that occurred when adding the dry cyclone dust to the wet centrifuge cake being conveyed to the dryer. These two materials when admixed often "set-up" and stalled the conveyor.

G) The MgO slurry system was further improved by the addition of a pre-mix tank at the discharge of the MgO weigh belt (G-103) to act as a steam seal between the now heated MgO slurry tank (G-102), and the enclosure erected directly over the tank housing the weigh feeder. This eliminated the problems associated with condensing water vapors in this dusty area, but created new ones because of frequent pluggage of the pre-mix tank.

H) The problem of frequent shutdowns of the calciner on false flame failure signals, because of the high dust level in the calciner, was solved by by-passing the flame scanning equipment. Operator control is substituted for this instrumentation after the kiln refractory becomes heated to the ignition temperature.

I) Additional improvements were made in the calciner feed system. A vibrating bin bottom was installed on G-506, and the MgSO_3 weight belt G-514 changed to a more robust unit with faster response to varying feed bulk density.

3. In the third category, these other modifications made were:

A) Conversion of the MgSO_3 bucket elevator (G-511) at the regeneration plant from a centrifugal discharge to a continuous machine allowing it to handle either dusty or granular material.

B) Installation of a tail gas scrubber at the acid plant to reduce emissions to the new standards was completed and the system operated. The acid plant

itself is of an old design for 95% conversion, and was in the process of being phased out before the program started, because of the inability of such plants to meet the new standards of the Federal Clean Air Act. In order to continue the program in compliance with these standards, a caustic (NaOH) scrubbing system incorporating a venturi absorber of Chemico's special design was installed to treat the acid plant's emissions, reducing the SO₂ from 3000 ppm to 300 ppm.

4.4. SYSTEM AVAILABILITY

System availability for the flue gas desulfurization system installed at Mystic Station is given in Table 9 which summarizes operating time and availability by program period and shows the improvement in availability during the 4,127 hours of operation logged with the system treating flue gas from a high sulfur fired boiler. Table 10 presents the data on a monthly basis, with comments on the primary causes for reduced availability during the planned operational testing and continuous operation phase which comprised the final year of the program.

The continuous operation phase was interrupted repeatedly by boiler outages resulting from numerous tube failures unrelated to the FGD system. Because of the problem, the maximum duration of continuous gas flow to the absorber was limited to a week at a time, however, during April, May and June, two periods of 35 and 30 days were obtained with essentially 100% availability despite the numerous boiler failures. This demonstrated the ability of the FGD system to cycle with both load and varying operation of the boiler. This is shown in Figure 15 which depicts periods of FGD system operation, average load during those periods and causes of absorber system outage.

Similar data are not presented for the regeneration plant as most outages there were caused by interruptions in the MgO supply and these, except for two cases, resulted from breakdown in the transportation and trucking operation. In the other two instances, first the national shortage of petroleum products in November 1973 forced the regeneration plant out of service for several weeks until this situation was resolved and a fuel oil supply for the calciner secured; and second, a two week regeneration plant outage was forced by a failure in a piece of acid plant equipment not related to the calcination system. Several problems were encountered and

TABLE 9

FLUE GAS DESULFURIZATION SYSTEM AVAILABILITY
BY TEST PROGRAM PHASE

<u>Description</u>	<u>Period</u>	<u>Operating Hours</u>	<u>Availability</u>
Pre start-up through Break-in period	April 1972 to May 1973	1,127	17%
Planned Operational Testing	June 1973 to February 1974	1,630	46%
Continuous Operation*	March 1974 to June 1974	1,370	76%

* During the period 3/1/74 to the end of the program, the Mystic 6 boiler only operated at total of 1,721 hours because of numerous boiler tube failures.

TABLE 10

FLUE GAS DESULFURIZATION SYSTEM AVAILABILITY

<u>Month</u>	<u>Availability</u>	<u>Comment</u>
June 1973	68%	
July	61%	
August	--	Boiler annual overhaul
September	38%	
October	60%	System availability decreased during the last part of the year due to heavy erosion/corrosion attack in the recycle slurry piping system.
November	26%	
December	13%	
January 1974	28%	System availability limited by boiler related problems which caused frequent shut downs in January and February
February	25%	
March	87%	
April	81%	
May	57%	Low availability in May due to two week acid plant outage
June	80%	Program termination.

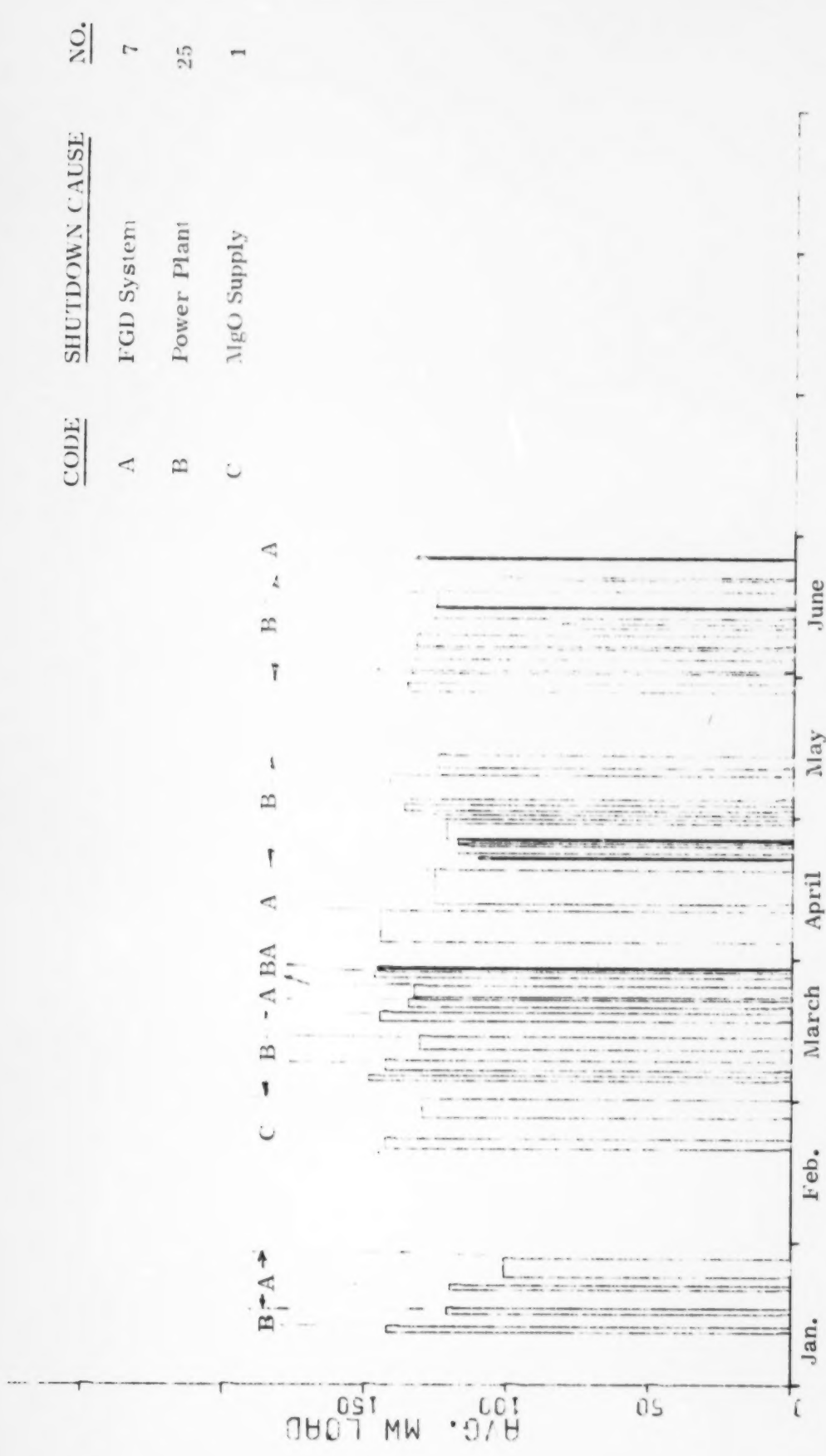


FIG. 15
 BOSTON ED. OPERATIONS JAN. - JUNE 1974
 FLUE GAS DESULFURIZATION SYSTEM OPERATING PERIODS AND OUTAGES

solved at this plant as detailed in the foregoing section (Sec. 4.2) on the operation, and in addition the calciner was never run at its design capacity; however, the supply of regenerated magnesia was maintained at satisfactory levels when the plants were operating as an integrated system.

5.0 EQUIPMENT ARRANGEMENT AND MATERIALS OF CONSTRUCTION

Figure 16 shows the general arrangement plan for the flue gas desulfurization system installed at Boston Edison Company's Mystic Station and identifies the location of the major pieces of equipment. In the SO₂ absorption system, a wide variety of conditions exist in the equipment as the process streams range from incoming flue gas to saturated gas streams, liquid and slurry streams, and varieties of solid chemical compounds. A range of acidity also exists throughout the plant. Figure 17 shows the general arrangement of the regeneration plant at Rumford, R.I. and also shows major equipment location. Tables 11 and 12 list the equipment by category, and material of construction for both plants. Comments are given if problems were encountered with a particular item.

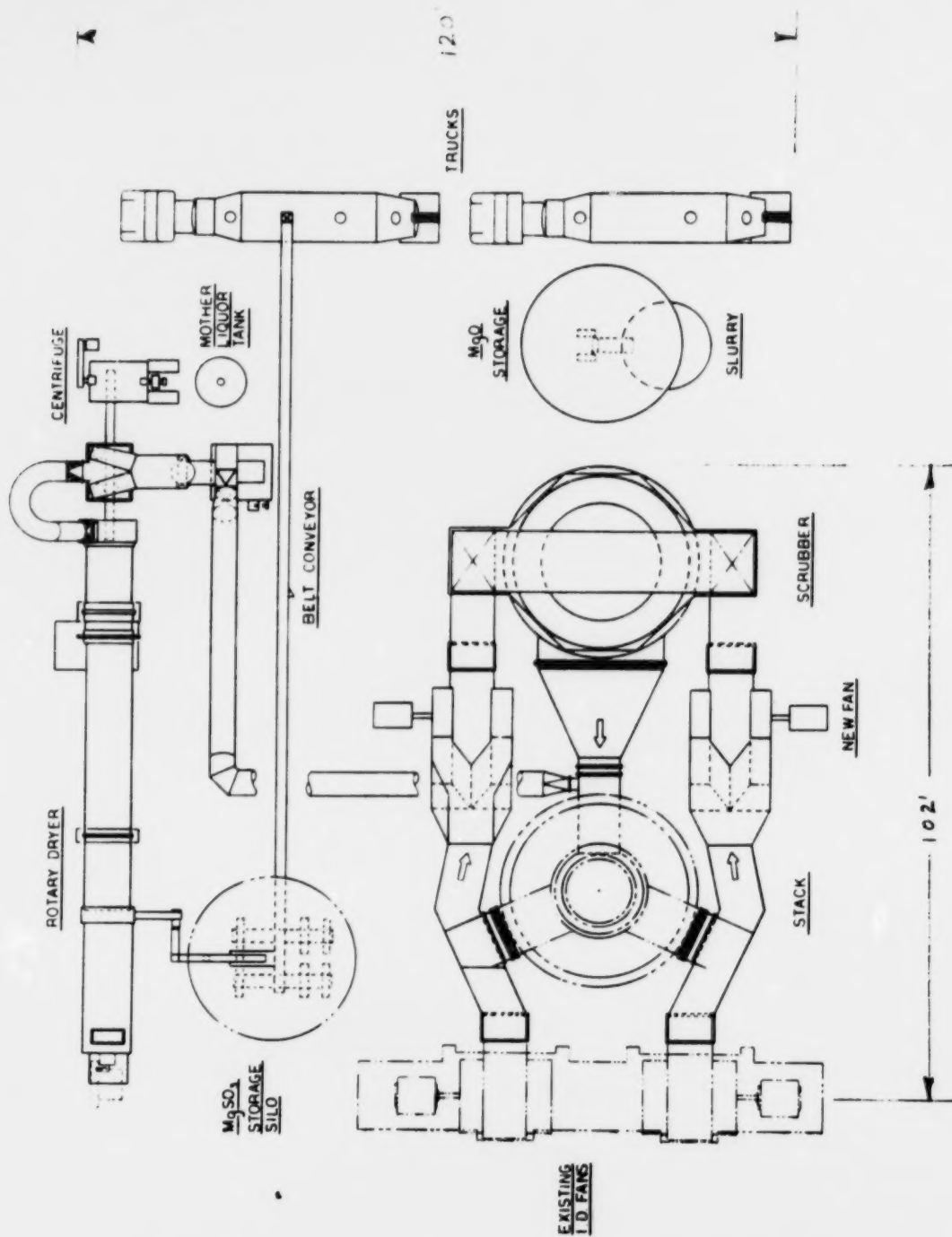


FIG. 16
 GENERAL ARRANGEMENT—PLAN
 SCRUBBING SYSTEM FOR 155 MW CAPACITY AT MYSTIC NO. 6 STATION OF
 BOSTON EDISON COMPANY

TABLE 11

EQUIPMENT PERFORMANCE

FLUE GAS DESULFURIZATION SYSTEM

<u>Code No.</u>	<u>Equipment</u>	<u>Material Of Construction</u>	<u>Comment</u>
D-401	Combustion Chamber	Refractory Lined Carbon Steel	Two outages resulted from a failure of the burner block and resultant failure of the refractory lining adjacent to it.
G-102	MgO Makeup Tank	Carbon Steel	Steam sparging of the tank and a pre-mix unit were added; an 18 in. standpipe was also added at the outlet nozzle after plugging of the outlet of the vessel by MgO lumps.
G-301	Mother Liquor Tank	Carbon Steel	Satisfactory Operation
I-101	MgO Storage Bin & Dust Collector	Carbon Steel	Satisfactory Operation
J-101	MgO Makeup Pumps	Cast Iron	Severe erosion of impellers and casing was experienced.
J-201	Recycle Pumps	Cast Iron	Severe erosion of pumps was experienced.
J-301	Mother Liquor Pump	Cast Iron	Some impeller erosion was experienced.
K-201	ID Booster Fans	Carbon Steel Wheel Mild Steel Case	Some corrosion of case was corrected by precrete lining the lower half of the case.
K-401	Dryer ID Fan	Carbon Steel	Satisfactory Operation
K-402	Dryer FD Fan	Carbon Steel	Satisfactory Operation

TABLE 11 CONT'D

<u>Code No.</u>	<u>Equipment</u>	<u>Material Of Construction</u>	<u>Comment</u>
M-101	MgO Tank Agitator	304 SS wetted parts	Satisfactory Operation
M-301	Mother Liquor Tank Agitator	304 SS wetted parts	Satisfactory Operation
O-101	MgO Conveyor	Aluminum Straight Tube SS Bend	A hole developed in the bend after one year of service.
O-102	MgO Vibrating Hopper	Carbon Steel	Satisfactory Operation
O-103	MgO Weighing System		Frequent shutdowns caused by jamming of the weigh control mechanism and belt.
O-401	Dryer	Carbon Steel	Numerous problems primarily of a process nature caused by adherence of centrifuge cake to dryer walls.
O-402	Dryer Conveyor	Carbon Steel	Frequent shutdowns caused by hardening of centrifuge cake with subsequent jamming of the unit and wear of the unit.
O-403	MgSO ₃ Conveyor #1	Carbon Steel	Occasional large lumps from dryer jammed conveyor.
O-404	MgSO ₃ Elevator	Carbon Steel	Satisfactory service except for one outage because of a bearing failure on the drive sprocket.

TABLE 11CONT'D

<u>Code No.</u>	<u>Equipment</u>	<u>Material Of Construction</u>	<u>Comment</u>
O-405	MgSO ₃ Conveyor #2	Carbon Steel	Eliminated from material handling train.
O-406	MgSO ₃ Weigh Feeder		Eliminated from material handling train after numerous failures.
O-407	MgSO ₃ Screw Feeder	Carbon Steel	Satisfactory Service
O-408	MgSO ₃ Belt Conveyor	Rubberized Belt, Conventional drive mechanism	Trouble free operation, however, dusty nature of feed created secondary clean up problem.
¹ 2 1 O-409	Dust Feeder	Carbon Steel	Entire dryer dust handling system was revised as part of dryer modifications.
R-402	Dust Collector	Carbon Steel	Trouble free operation except for some instances of packing of collected dust in hopper after failure of O-409.
R-301	Centrifuge	Carbon Steel	See Sec. 5.2.

TABLE 12

EQUIPMENT PERFORMANCE

REGENERATION SYSTEM

<u>Code No.</u>	<u>Equipment</u>	<u>Material Of Construction</u>	<u>Comments</u>
E-501A, B	Weak Acid Cooler	316 SS	Satisfactory Service
F-502	Weak Acid Stripping Tower	Chemical Stoneware	Satisfactory Service
G-501	Weak Acid Pump Tank	Reinforced Fiberglass Polyester.	Satisfactory Service
G-505	Coke Feed Bin	Carbon Steel	Satisfactory Service
G-506	MgSO ₃ Feed Bin	Carbon Steel	Plugging problem corrected by installation of a vibrating bin bottom.
G-507	Bearing Water Pump Tank	Carbon Steel	Satisfactory Service.
G-508	Air Receiver	Carbon Steel	Satisfactory Service
I-502	MgO Silo	Carbon Steel	Satisfactory Service
J-050A, B	Recycle Water Pumps	Alloy 20	Satisfactory Service
J-501A, B	Calciner Fuel Oil Pumps	Cast Iron	Satisfactory Service
J-502A, B	Weak Acid Circulating Pumps	Alloy 20	Satisfactory Service

TABLE 12 CONT'D

<u>Code No.</u>	<u>Equipment</u>	<u>Material Of Construction</u>	<u>Comments</u>
J-503	Neutralizing Pump	Natural Rubber Lined	Rubber swelled and bound pump after two years operation.
J-504	Bearing Water Pump	Cast Iron	Satisfactory Service
K-501	Calciner F.D. Fan		Satisfactory Service
O-503	MgO Conveyor #1	Carbon Steel	Frequent hanger bearing failure.
O-504	MgO Elevator	Carbon Steel	Wear of sprockets and chain experienced after 18 months, unit converted to continuous discharge type.
O-505	MgO Conveyor #2	Carbon Steel	Satisfactory Service
O-506	MgO Vibrating Hopper	Carbon Steel	Satisfactory Service
O-508	MgO Weigh Feeder		Eliminated from material handling train after numerous failures.
O-509, O-510	MgSO ₃ Conveyor #1	Carbon Steel	Problems limited to bearing failures.
O-511	MgSO ₃ Elevator	Carbon Steel	Frequent break downs required shaft size increase.

TABLE 12 CONT'D

<u>Code No.</u>	<u>Equipment</u>	<u>Materials Of Construction</u>	<u>Comments</u>
O-512	Calciner Conveyor	Carbon Steel	Satisfactory Service
O-513	Calciner Elevator	Carbon Steel	Unit converted to continuous discharge type, bucket fastening bolts failed due to corrosion.
O-514	MgSO ₃ Weigh Feeder		Numerous failures, unit replaced by a BIF unit reducing the number of break downs.
O-515	Coke Weigh Feeder		Belt tracking problems.
O-516	Cyclone Dust Feeder		Satisfactory Service
O-523	MgSO ₃ Airveyor	Carbon Steel	Frequent pluggage due to tramp material and lumps in transported MgSO ₃ .
P-075	Cyclone Dust Collector	316 SS	Satisfactory Service
R-401	Fuel Oil Supply & Combustion Equipment,		Problem of unsuitable flame failure control.
R-501	Calciner	Carbon Steel, Refractory lined	A two foot wide section of the refractory lining loosened and failed, pinion gear failed after two years.
R-020	WA Venturi Scrubber	316 SS	Occasional pluggage due to formation of elemental sulfur.

5.1 ABSORBER SYSTEM AREAS SUBJECT TO CORROSIVE ATTACK

Carbon steel is the principal material of construction of the unit but because of SO_2 absorption, the carbon steel must be protected. In some cases stainless can be substituted in the internal structure, but here the corrosion problem can be influenced by the amount of chlorides in the recycle stream (Table 13). Since temperatures in the FGD System are normally low, (the adiabatic saturation temperature of the gas) as long as scrubbing liquor is present, the carbon steel structural and other parts of the venturi absorber were protected by about 60 mils of glass reinforced polyester resins. This material was chosen over stainless as the concentration of chlorides in the absorber slurry could increase up to a point where Austenitic stainless steels are susceptible to stress cracking and sulfuric attack in the presence of high chloride causes alloys like type 316 to pit excessively.

Some wear was experienced in the absorber during the twenty-seven months' operation of the plant. The extent of this wear was minor, limited to the erosion of the top coat of the two layer application of the FRP liner, and the erosion of the steel apex of the toroidal ring.

The pattern of the erosion of the torus indicated it occurred in the areas of over-lap of the adjacent irrigation sprays. Repair was easily accomplished by welding an angle section over the damaged areas of the torus. This can be seen in Figure 18 which shows (from left to right) the inner core, first slot, torus, second slot, part of the converging wall, and the tips of two spray nozzles.

The shaded areas on the converging section of inner wall are the underlayer of the FRP liner. The patched area of the torus is visible.

The polypropylene chevron modules, used for mist eliminators, have shown no corrosion problems, nor have the plastic beams used to hold them down. The upper surface of these modules is shown in Figure 19.

Recycle pumps and piping have been subject to extensive wear of an erosive-corrosive type. This was particularly serious in areas of high velocity and turbulence. The recycle pumps were originally all carbon steel. Figure 20 shows the

TABLE 13
CHLORIDE ANALYSIS

	CHLORIDE %
Scrubber Slurry (11/16/73)	0.21%
Magnesium Oxide (New)	0.16 - 0.18
Magnesium Oxide (Regenerated)	0.0
	CHLORIDE (PPM)
Process Water (Avg. 1972)	10.4 PPM
Process Water (12/6/73)	7.8 PPM
Process Water (12/7/73)	3.4 PPM

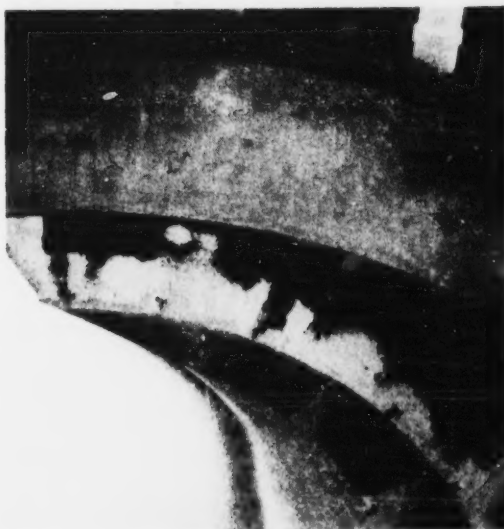


Fig. 18
VENTURI THROAT AREA WEAR

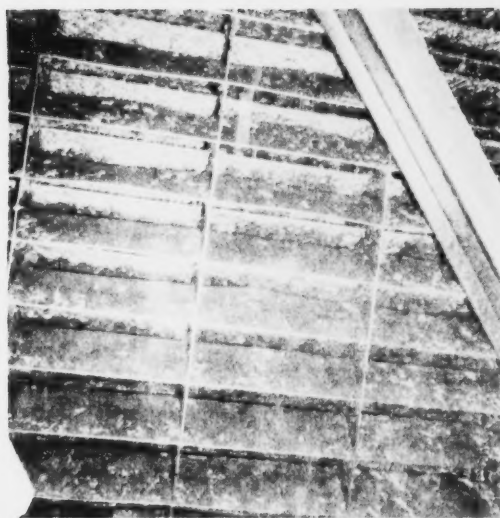


Fig. 19
DEAERATOR MODULES



FIG. 20
RECYCLE PUMP IMPELLER WEAR

condition of the carbon steel impellers after one year of service. The impellers, suction plates, and other parts of the pumps were replaced in stainless steel, where available; however, these were also subject to wear when used in the slurry service.

Similar wastage of metal due to abrasion was experienced in the MgO slurry pumps. Leaks also developed in sections of the distribution piping of the recycle lines shown in Figure 21. A sample was cut from a larger diameter header pipe which had welded to it, in a horizontal plane a smaller 4-1/2 inch diameter pipe and sent to L. Pitkin, Inc., analysts and metallurgists, for evaluation. This pipe had been weld repaired where it had holed through on a prior occasion. In the sample submitted there were two holes, approximately opposite each other near the weld joint, at an angle of about 45° to the cylindrical axis of the larger pipe.

The following is a report of the examination.

(Figure 22 is a photograph of the T-section sample as received, viewed so as to show one of the areas where the smaller pipe had holed through).

"The outer surface of the sample showed flaked paint and rust staining, and except for the holes, appeared to be in sound condition. The inner surface of the sample was examined and it was observed that there was extensive, severe deterioration at the weld joint. The deterioration diminished proceeding away from the joint towards the flame-cut end of the small pipe. Deterioration was concentrated for about 180 degrees on one side. The other side was, by comparison, relatively sound.

"Further examination showed the I.D. of the small pipe to have thinned rather gradually and uniformly on one side as revealed by a cross-section cut about five inches from the weld joint. There were no accompanying irregularities as were present near the weld joint. The cut cross-section is shown in Figure 23.

"Microspecimens were prepared through the deteriorated area of side A of the small pipe. The material at the I.D. merely showed smooth undulations with no corrosion penetration. The microstructure was comprised of pearlite and

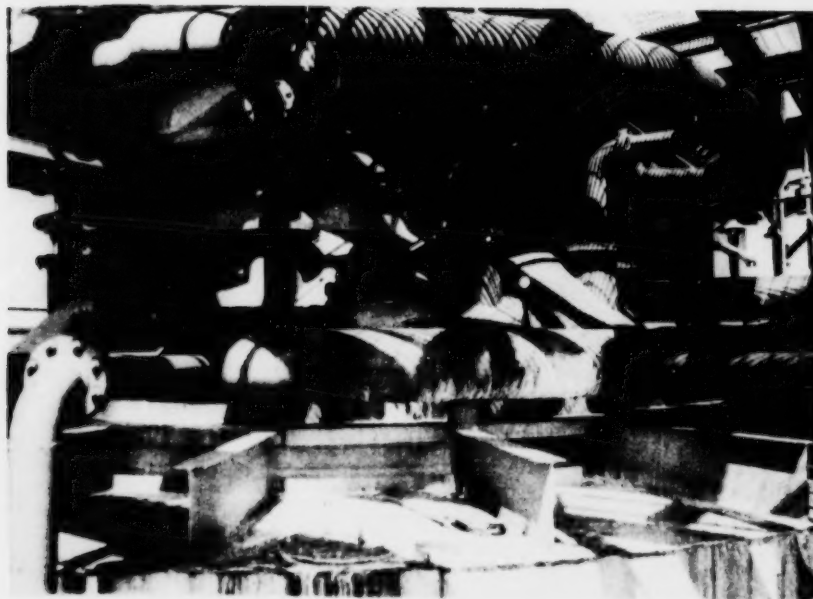
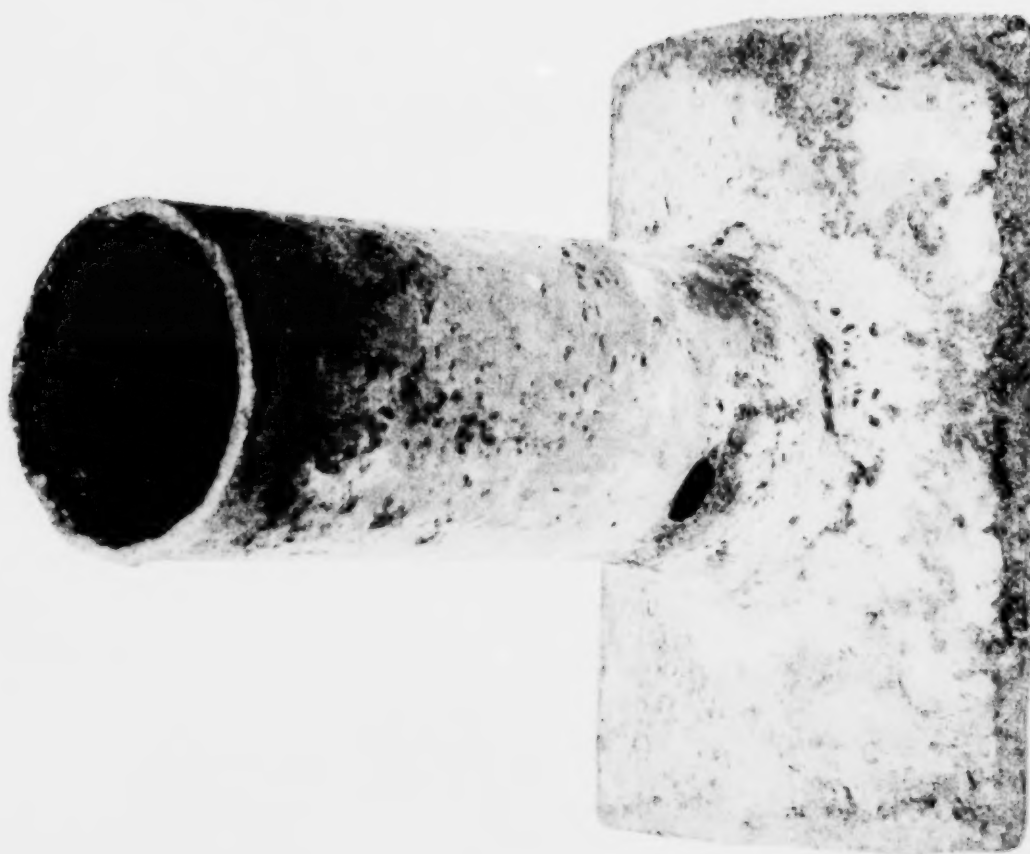


Fig. 21
RECYCLE PIPE-UPPER SECTION



"T" SECTION OF RECYCLE LINE

FIG. 22.

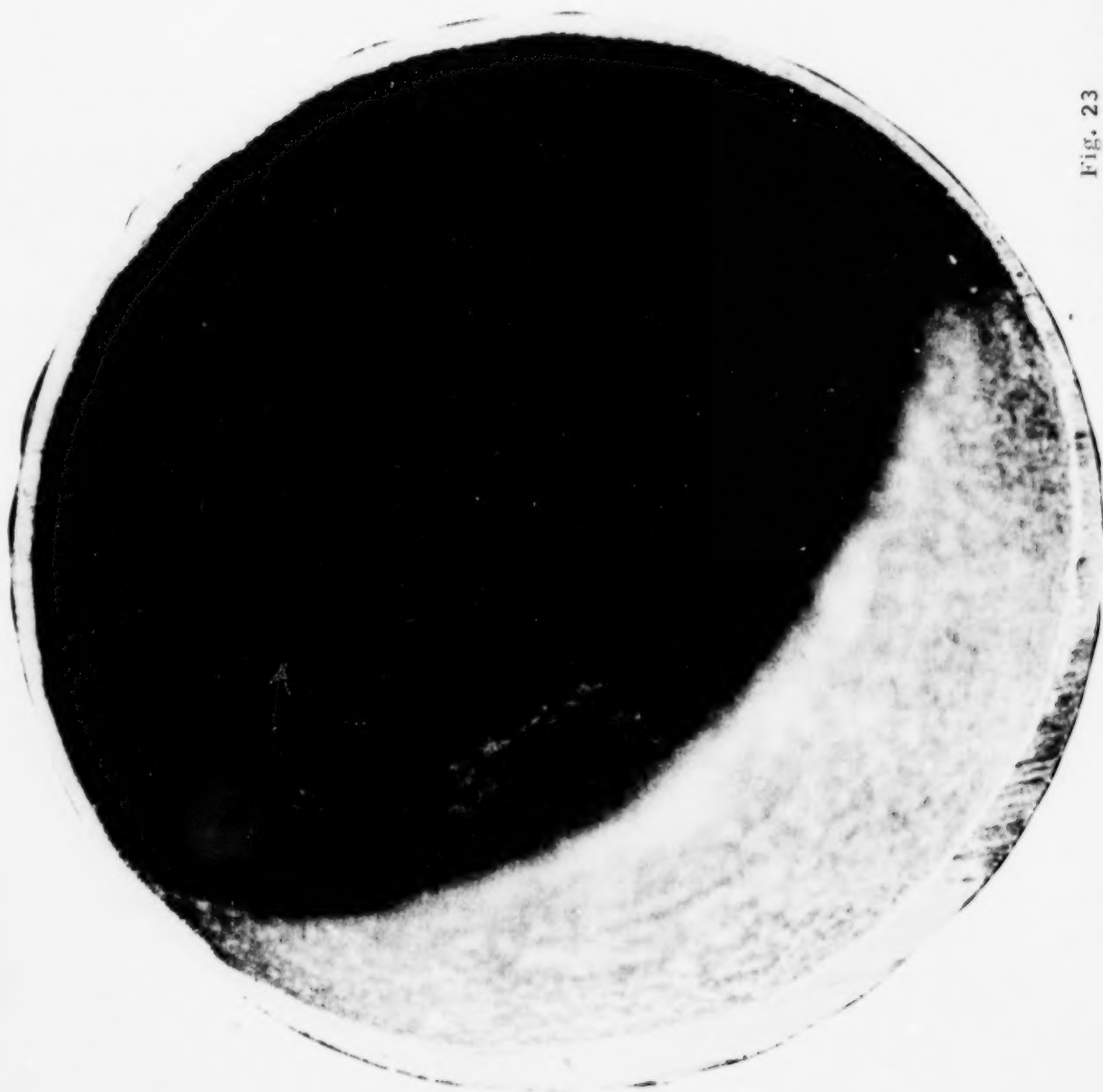


Fig. 23
CROSS SECTION OF RECYCLE PIPE

ferrite in a slightly acicular or needle-like pattern characteristic of normalized medium carbon steel (estimated 0.25% carbon). Figure 24 is a photomicrograph at 100X showing the general microstructure and I.D. profile in the deteriorated area where the wall had been considerably reduced.

"The rust and corrosion product on the I.D. surface of the pipe was leached with distilled water and checked for acidity by acid test paper. The results indicated a pH of from 6 to 7 - virtually neutral. The leachings were further checked for sulfites and sulfates which, if present, would be acidic in nature and, of course, could progressively attack the carbon steel. The results were negative - neither sulfates nor sulfites being found.

"It would appear that any sulfate or sulfite compounds that were present on the inner surface had been washed away in subsequent operation or perhaps converted to water soluble compounds and so not detected. In any event, the inner surface of the T-sample was in a potentially uncorrosive condition with respect to the slurry handled at the time it was received.

"The deterioration sustained was only in the small diameter pipe. This was a thinning on one side of the pipe diminishing towards its discharge end. The large diameter pipe was virtually unaffected. This condition, in the metallurgist's opinion, was the result of inlet end impingement erosion. Liquid flow over the sharp 90-degree change in direction into the smaller diameter discharge pipe line causes eddies and whirls due to the abrupt change in flow direction and increased velocity. The result is that there is a mechanical erosion effect accompanied by differential aeration of the solution with attendant formation of galvanic oxygen concentration cells which leads to an accelerated deterioration as observed."

The recycle line wall thickness was gauged using ultrasonic testing revealing that there had been general corrosion throughout the system. A possible cause of the corrosion is the presence of the bisulfite ion (HSO_3) which persists up to a pH of 8.3 (Figure 25) i.e., above the normal system operating pH. Another contributing factor for corrosion were short periods of low pH excursion which occurred during the course of the program because of control upset.

March 4, 1974
M-3070

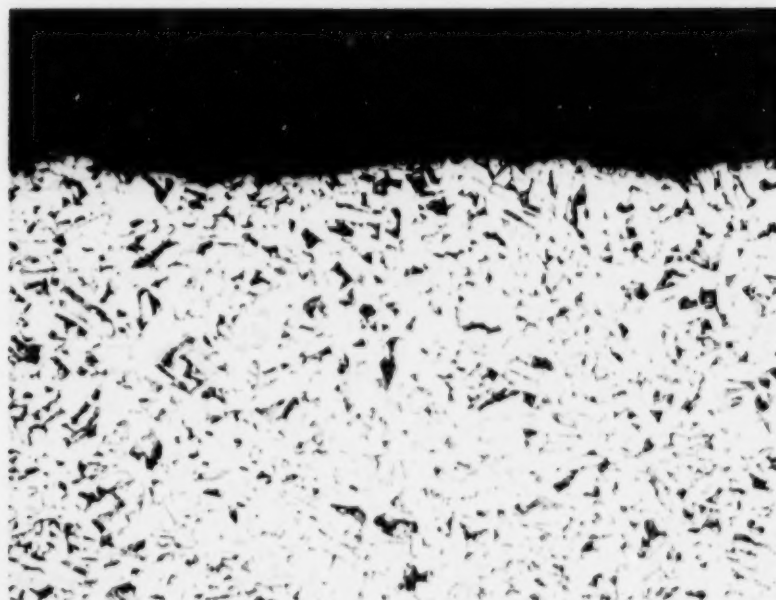


FIG. 24

MICROSTRUCTURE AT I.D. SURFACE -
DETERIORATED AREA

100 X

Photomicrograph of longitudinal section through deteriorated area, side A, of small diameter pipe showing general microstructure of ferrite and pearlite. The I.D. surface profile (top) shows a smooth undulating profile with no corrosion penetrations and absence of any oxide scale build-up.

The microstructure is normal for a plain medium carbon steel.

NEUTRALIZATION CURVE M₃O

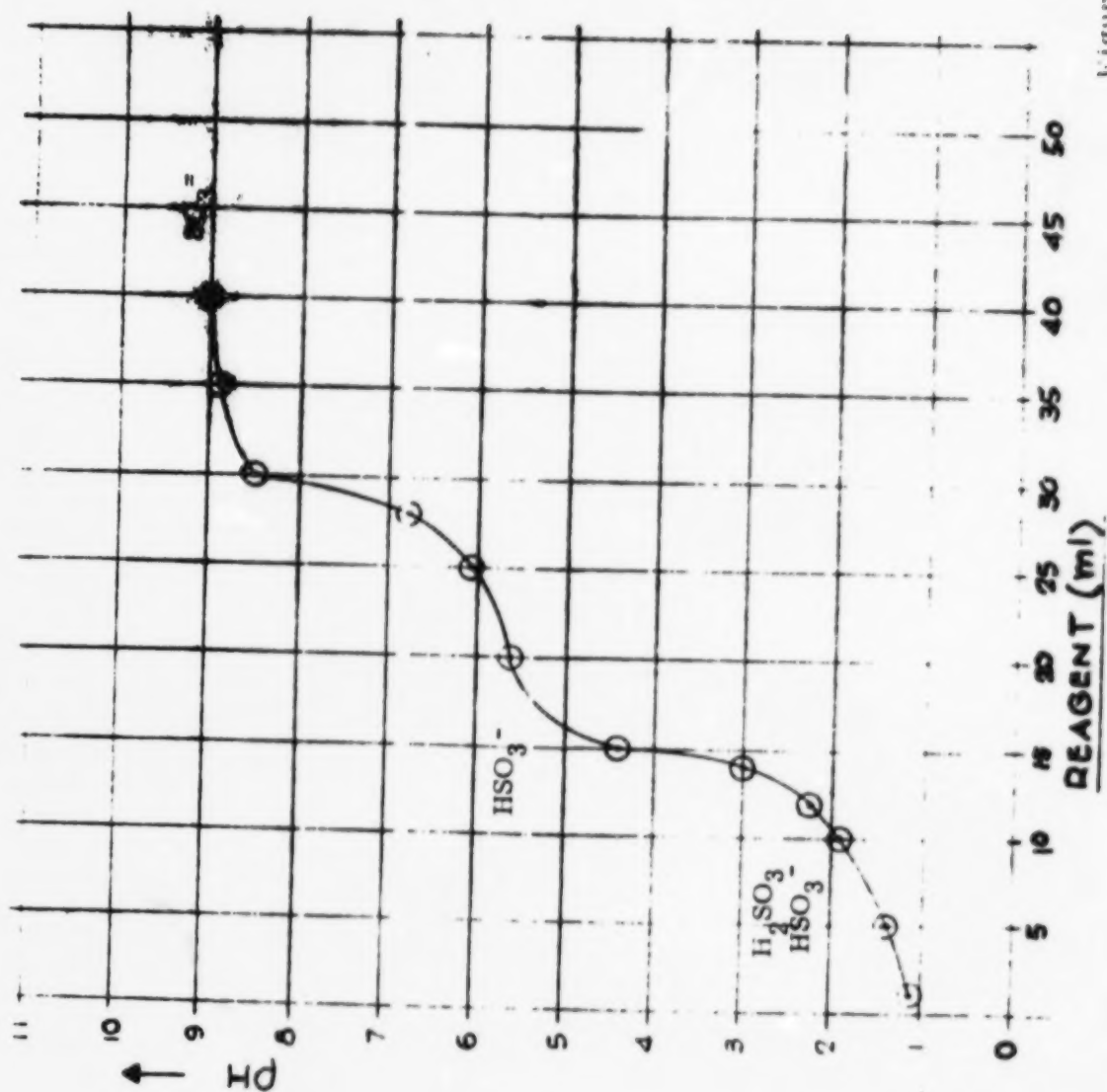


Figure 23

5.2 CENTRIFUGE SYSTEM

Sections of the centrifuge are also subject to wear and in this case it appeared that abrasion was the cause of wastage of metal. The parts of the machine which were most affected were the replaceable items such as bowl plows, and conveyor flights. The unit, of carbon steel construction, had the conveyor flights originally edged with Colmonoy #6. After the first 14 months of intermittent service, the machine was disassembled and inspected with the following observations:

Conveyor Blades

Conveyor blades were found to be worn an average of $3/32$ " in the cylindrical section to a maximum of an average 1" in the conical section. Conveyor blades were worn thin in the areas adjacent to the feed ports. Badly worn blade segments were replaced and the blade areas adjacent to the feed ports were covered with J alloy. Conveyor blades were built up and re-hardsurfaced with Colmonoy #6, which was the original hardsurfacing alloy.

Product Build-Up

It was determined upon inspection that the out-of-balance problems reported were probably caused by build-up of solids in the drain compartment of the conveyor hub. Virtually all surfaces of the bowl and conveyor had a significant build-up of hardened solids resembling concrete. In order to minimize solids this build-up in the conveyor hub drain compartment, a tube was installed to blank-off this zone. All accessible surfaces of the bowl and conveyor were then covered with Tropolite plastic coating to provide a smooth corrosion resistant surface.

Bowl Head, Bowl Head Plows & Wiper Beads

Considerable wear was evident in the solids discharge area. The hardfaced product wiper beads on the bowl head periphery were worn off and the bowl head flange had worn approximately $1/2$ " radially. The bowl head solids plows evidenced considerable wear. The bowl head was repaired and the wiper beads were replaced and an additional eight (8) beads were applied. Two of the solids plows were replaced

by the larger diameter case plows and the remainder of the bowl head plows were re-hardsurfaced and reinstalled.

The above summary while not complete does highlight the important steps taken to improve the reliability of the equipment.

As noted, the conveyor was re-hardsurfaced with the original (Colmonoy) metal, as were the bowl head plows. Two of the solid plows were replaced with larger diameter case plows and the machine returned to service. The hard-surfacing was touched up in October 1973, when the machine was disassembled for repair to its feed pipe and the installation of additional wash nozzles.

The machine was again opened and inspected in January 1974 and wear was still evident in the conveyor (Figure 26). It was hardsurfaced with Stellite II and remained in service until the end of the program.

Total time during which the centrifuge was fed in the periods is summarized in the following table:

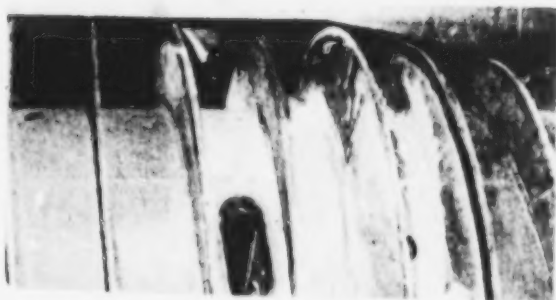
TABLE 14

<u>Start</u> _____	<u>Finish</u> _____	<u>Hours Fed</u>	<u>Equivalent Days</u>
April 1972	June 1973	1127	48.9
August 29, 1973	Sept. 25, 1973	215.5	9
Sept. 30, 1973	Jan. 28, 1974	818.6	34.1
Feb. 19, 1974	June 26, 1974	1448.1	60.3

A plot of the conveyor wear is given in Figure 28, which graphically shows the similarity of wear patterns with the feed to the machine entering between blade 14 and 15. It is also evident that the Stellite II applied in the latter part of the program gave improved service (blade wear would have to exceed two inches before a significant reduction in efficiency would be experienced). Based on the rate of wear for the period February through June 1974, it appears that over one year of continuous operation would be obtained



Centrifuge Conveyor
(Jan., 1974)



Showing Flight Wear

FIGURE 26

Centrifuge Conveyor
(Jan., 1974)
Showing Scale Build-up
on Flights



FIGURE 27

BIRD CENTRIFUGE CONVEYOR BLADE WEAR

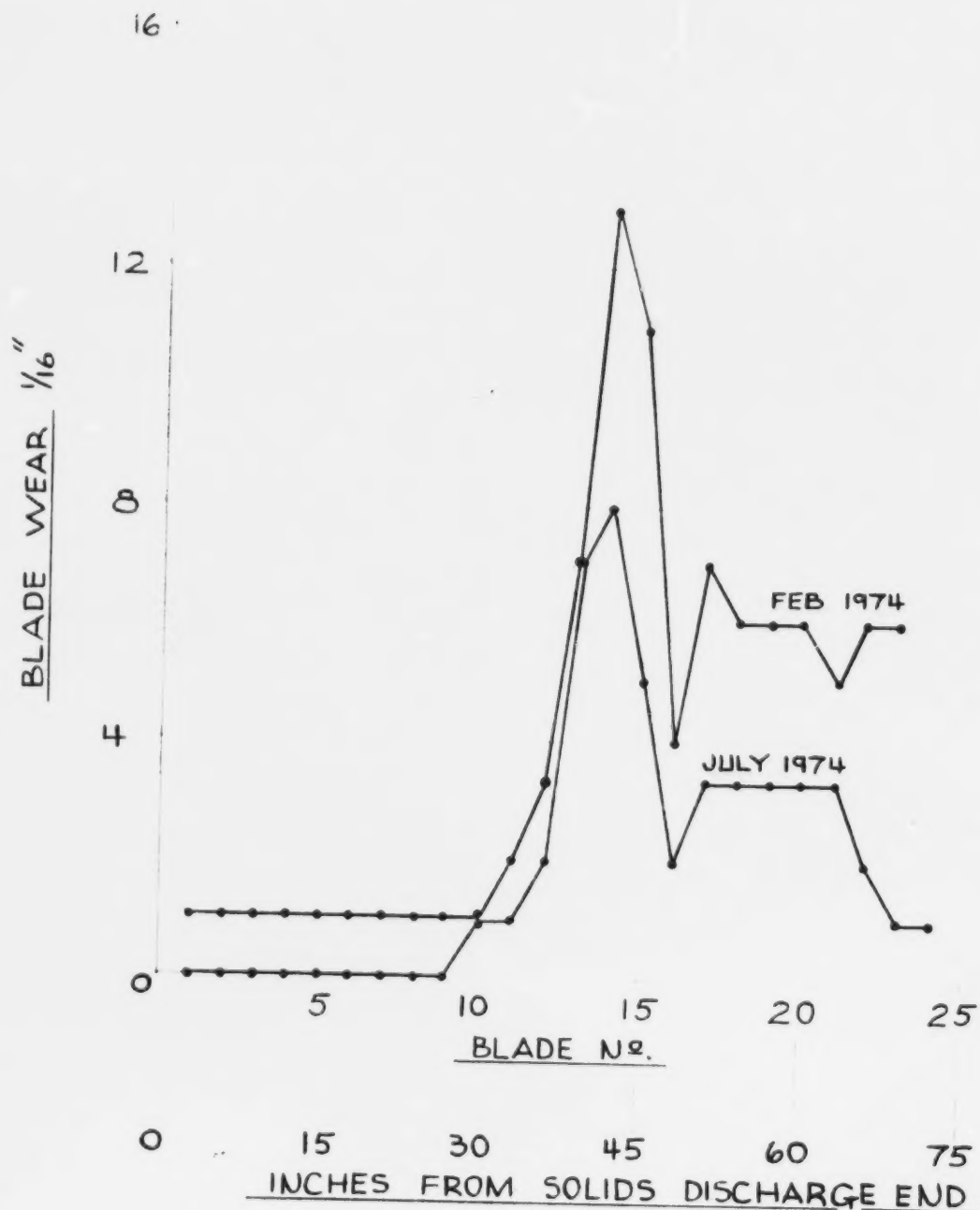


Fig. 28

SCALE 6"=1"

before the conveyor would have to be repaired.

5.3 STACK

The existing Mystic #6 stack handled dryer off gas for an eight month period in addition to the flue gas. The stack was brick lined, with concrete outer shell, 335' high with 15' inside diameter at the base of the inner stack. It is designed to withstand saturated, acidic gases with the inner stack constructed of solid shale brick laid up in a potassium silicate mortar (Corlock). The recommended pH range of the mortar is 1 to 7 where there is no submergence, and 1 to 5.5 where there is submergence or heavy liquor flow.

The stack was inspected on several occasions. The first inspection, prior to redirecting the dryer-off gas to the absorber, revealed several inches of build-up of solid magnesium salts in the stack. These were washed off in a clean-down of the stack and no significant deterioration of the brick work or mortar was observed after the washing. After the dryer off-gas was treated in the absorber with the flue gas there was no reoccurrence of the problem.

On a second occasion, the inner stack was observed to be leaning and touching the outer shell at its top where a ten foot vertical section of the inner brick stack had cracked. (During this period construction of Unit 7 was underway, including pile driving in the area immediately adjacent to the absorption plant and stack).

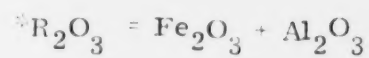
After the dryer-off gas was redirected to the absorber, consideration was given to reheating the treated flue gas. However, inspection had shown no evidence of deterioration of the stack due to the condensing liquor (Table 15), and there was no observation of "raining" from the stack during operations with the SO₂ Absorption System. No reheat was provided for the flue gas except for that resulting from the mixing of the small portion of untreated gas during the last four months of operation.

5.4 REGENERATION SYSTEM

With few exceptions, the materials of construction selected for the calciner installation proved to be entirely satisfactory. Problems listed below resulted from operating

TABLE 15
STACK DRAININGS ANALYSIS

	6/13/73	7/17/73	7/18/73
Load	145 MW	145 MW	145 MW
pH	4.1	4.3	3.3
SO ₄ (As MgSO ₄)	13.3%	7.0%	5.3%
Ni	0.01%	0.004%	0.003%
R ₂ O ₃ *	0.12%	0.18%	0.22%



conditions which were not anticipated in the original design.

All material handling equipment for the dry solids, both feed and product, are of carbon steel. No corrosion problems were experienced, with the exception of the coke bin. The coke originally purchased contained from 10% to 17% free moisture. Since coke was seldom used, some scaling took place on the walls of the coke bin. Even so, the problem was not one of deterioration of the bin, but rather that scale would occasionally break off in large pieces and cause malfunctions of the coke feeder.

No corrosion problems were observed in the calciner elevator despite the fact that it would frequently become wet with condensate from combustion gases. This occurred when the calciner was not being fed but the burner was kept on to maintain temperature.

The gas duct between the calciner and the venturi scrubber was constructed of Type 310 stainless steel in anticipation of high exit gas temperatures. The venturi scrubber itself was constructed of Type 316 stainless steel. Both these areas were subject to corrosion under certain conditions. In places where moist solids would accumulate there was considerable corrosion. This was evidenced by numerous perforations in the convolutions of the Type 310 expansion joints, in the bottom portion of horizontal or inclined runs of the Type 310 ducts, and in the Type 316 sampling system for the analyzer monitoring the oxygen content of the calciner exit gas. However, if the metal surface was clean and dry, or if it was constantly washed with a liquid stream as in the scrubber, no corrosion was experienced.

The gas duct from the venturi scrubber to the acid plant drying towers was constructed of fiberglass reinforced polyester and was satisfactory.

The first 40 feet of the calciner was lined with 9 inch of high alumina (70%) fire brick, and the remaining 80 feet with 6 inches of high duty kiln block, backed with 2½ inches of insulating brick. The high alumina brick showed no evidence of degradation. The kiln block suffered only a few

spalled corners, except in the area located from 25 feet to 40 feet from the feed end. In this area, considerable spalling of the face of the block took place. It is possible that in this area, most of the combined moisture is released from the feed. In this case, the face of the lining is subjected to rapid temperature fluctuations as feed is introduced or stopped, or as the moisture content of the feed changes.

The insulating brick behind the block was relatively soft. On two occasions, one or more rings of block fell out and considerable wear was found on the insulating brick.

This wear allowed the block to move outward toward the shell.

5.5 CORROSION SAMPLES

Coupons of various metals and coatings were placed in the system at the initiation of testing in a program of evaluation of materials of construction. Results for two of these test racks are given below:

- 1) A test rack of various metals was immersed in the venturi absorber basin and removed after approximately eight months of exposure. Table 16 shows the corrosion rates measured.
- 2) A test rack of coupons with various coatings was immersed in the mother liquor tank, an environment similar to Item 1 above. The results of the test, after the coated specimens had been immersed for an eight month period is given in Table 17.

TABLE 16

CORROSION TEST DATA

Corrosive Media	Magnesium oxide slurry scrubbing liquor for SO ₂ removal from power plant flue gas.														
Location Of Specimens	Immersed in venturi scrubber liquid.														
Type of Test	Field Aeration. Moderate Agitation. Moderate														
Temperature	<table border="0"> <tr> <td>F Avg</td> <td>120</td> <td>Min</td> <td>100</td> <td>Max</td> <td>140</td> <td></td> </tr> <tr> <td>C Avg</td> <td>49</td> <td>Min</td> <td>38</td> <td>Max</td> <td>60</td> <td>File. 603</td> </tr> </table>	F Avg	120	Min	100	Max	140		C Avg	49	Min	38	Max	60	File. 603
F Avg	120	Min	100	Max	140										
C Avg	49	Min	38	Max	60	File. 603									
Test Duration	From 12/5/72 To 7/31/73 Total Days 238														

<u>Material</u>	<u>Corrosion Rate (MPY)</u>	<u>Maximum Pit Depth (MILS)</u>
SS EB 26 1	0.0	5
Incoloy Alloy 825	0.0	
Inconel Alloy 625	0.0	
Armco 22-13-5	0.0	
Allegheny Ludlum 6X	0.0	
Hastelloy Alloy G	0.0	
Hastelloy Alloy G	0.0	
Titanium	0.0	
SS Type 216	0.0	INCIP
SS Type 317	0.0	INCIP
Carpenter 20 CB-3	0.0	INCIP
Durimet 20	0.0	INCIP

TABLE 16 (CONT'D)
CORROSION TEST DATA

<u>Material</u>	<u>Corrosion Rate (MPY)</u>	<u>Maximum Pit Depth (MILS)</u>
SS Type 316L	0.0	
Hastelloy Alloy C-276	0.0	INCIP
SS Cast Grade CF8M	0.0	
Monel Alloy 400	5.0	13
Steel HSLA USS COR TEN	20.1	PERF 40
Steel AISI Type 1010	20.2	

TABLE 17 - RESULTS OF COATED SPECIMENS FROM CORROSION SPOOL
IN MOTHER LIQUOR BETWEEN CENTRIFUGE & PUMP

<u>TYPE COATING</u>	<u>GMS</u>	<u>COMMENTS</u>
CEILCOTE 103 PRIME +252 T.C.	-.20	EVIDENCE OF ABRASION AND SOME SLIGHT ATTACK, NOT AS GOOD AS FLAKELINE 103 ALONE.
CEILCOTE 103	0	NO EVIDENCE OF ATTACK
CEILCOTE 252	-.16	EVIDENCE OF ABRASION AND SOME SLIGHT ATTACK.
VAL CHEM TAR COAT	-.39	COATING PENETRATED ON SIDES OF SPECIMEN BUT NOT ON END WHERE THEY APPLIED HEAVIER COAT.
HI BUILD VINYL	-.02	VINYL COATING UNATTACKED. EVIDENCE OF CREVICE CORROSION UNDER TEFLON SPACERS.
HI BUILD EPOXY	-.19	SOME STAINING AND OBVIOUS CORROSION ATTACK.
CARBOGLAS (FIBER GLASS & POLYESTER)	-.46	SOME GLASS OBVIOUSLY MISSING. SPECIMEN SMOOTH INSTEAD OF ROUGH LIKE CEILCOTE COATINGS.
POLYURETHANE	-.35	COATING SHOWS HEAVY ATTACK.
CARBON STEEL	-16.28	BADLY SCALED AND HEAVILY ATTACKED.
LOCKPRIME - TUFCEM MEMBRANE	-.38	SOFT LIKE RUBBER, COATING CRACKED AND WORN AWAY, ALSO CREVICE CORROSION.

TABLE 17 CONTINUED - RESULTS OF COATED SPECIMENS FROM CORROSION SPOOL
IN MOTHER LIQUOR BETWEEN CENTRIFUGE & PUMP

<u>TYPE COATING</u>	<u>GMS</u>	<u>COMMENTS</u>
PLASITE 4000 (VINYL ESTER)	+.29	PICKED UP CONSIDERABLE FLY ASH WHICH WOULD NOT DESTROY COATING. COATING INTACT.
URETHANE ELASTOMER	-.09	SOME STAINING AND CHIPPING OF COATING AT EDGES, REST IN GOOD SHAPE.
CYANAPRENE ST-4808 (ELASTOMERIC URETHANE)	+.04	EDGES OF SPECIMEN WAS NOT COATED. COATING NOT ATTACHED BUT DOES NOT SHOW STAIN.
CARBON STEEL	-18.33	HEAVY SCALE AND WASTING AWAY OF SPECIMEN. ALMOST 20% MISSING FROM CORROSION.
GLASS REINFORCED VINYL ESTER	-.01	ATTACK ON ONE SIDE ONLY. OTHER SIDE STILL SHOWS MACHINING MARKS.

6.0 PROCESS CHEMISTRY

Pulverized solid magnesium oxide is introduced into a mixing tank where water is added and conversion to the hydroxide commences. The mixture is added as a slurry to the recycle stream of the venturi absorber to contact flue gas containing sulfur oxides and products of combustion. The reactions between magnesium hydroxide and sulfur dioxide produce principally magnesium sulfite.

The following series of reactions characterizes the principal ones of the process:

1. MgO Slaking:

$\text{MgO (s)} + \text{H}_2\text{O (l)}$	$\rightarrow \text{Mg (OH)}_2 \text{ (s)}$	(6-1)
$\text{Mg (OH)}_2 \text{ (s)}$	$\rightarrow \text{Mg (OH)}_2 \text{ (Soln)}$	(6-2)
$\text{Mg (OH)}_2 \text{ (Soln)}$	$\rightarrow \text{Mg}^{++} + 2 \text{ OH}^-$	(6-3)
2. SO₂ Absorbtion:

$\text{SO}_2 \text{ (g)}$	$\rightarrow \text{SO}_2 \text{ (Soln)}$	(6-4a)
$\text{SO}_2 \text{ (Soln)} + \text{H}_2\text{O}$	$\rightarrow \text{H}_2\text{SO}_3$	(6-4b)
$\text{SO}_2 \text{ (g)} + \text{H}_2\text{O}$	$\rightarrow \text{H}_2\text{SO}_3$	(6-4)
3. Formation of MgSO₃

H_2SO_3	$\rightarrow \text{H}^+ + \text{HSO}_3^-$	(6-5)
H SO_3^-	$\rightarrow \text{H}^+ + \text{SO}_3^{--}$	(6-6)
$\text{Mg (HSO}_3)_2 + 2\text{H}_2\text{O}$	$\rightarrow \text{Mg}^{++} + 2\text{OH}^- + 2\text{H}^+ + 2\text{HSO}_3^-$	(6-7)
$\text{MgSO}_3\text{XH}_2\text{O} + 2\text{H}_2\text{O}$	$\rightarrow \text{Mg}^{++} + 2\text{OH}^- + 2\text{H}^+ + \text{SO}_3^{--} + \text{XH}_2\text{O}$	(6-8)

X = 3 or 6
4. Other Reactions:

$\text{CO}_2 \text{ (g)} + \text{H}_2\text{O}$	$\rightarrow \text{H}_2\text{CO}_3$	(6-9)
H_2CO_3	$\rightarrow \text{H CO}_3^- + \text{H}^+$	(6-10)
H CO_3^-	$\rightarrow \text{CO}_3^{--} + \text{H}^+$	(6-11)
$\text{Mg CO}_3 \cdot 5\text{H}_2\text{O}$	$\rightarrow \text{Mg}^{++} + \text{CO}_3^{--} + 5\text{H}_2\text{O}$	(6-12)
H_2O	$\rightarrow \text{H}^+ + \text{OH}^-$	(6-13)

Kerr (1)* has presented the magnesia system equilibrium composition for a system at 125°F as follows:

<u>Component</u>	<u>Molality</u>
HSO_3^-	5.045×10^{-5}
H^+	2.416×10^{-4}
$\text{SO}_3=$	2.182×10^{-3}
Mg^{++}	2.452×10^{-2}
HCO_3^-	3.876×10^{-2}
$\text{CO}_3=$	2.920×10^{-3}
H_2SO_3	8.370×10^{-12}
H_2CO_3	1.108×10^{-4}
OH^-	3.808×10^{-5}

Sulfur dioxide partial pressure 1.651×10^{-11} atm.

Carbon dioxide partial pressure 6.493×10^{-3} atm.

Thus, from reactions (6-7) and (6-8) the SO_2 removal process is essentially an acid-base reaction, and the reaction in the liquid phase will be very rapid and almost quantitative.

While other side reactions take place the most significant are those which produce magnesium sulfate:



6.1 EFFECTS OF THE PROPERTIES OF MgO ON THE PROCESS

From equations (6-1) - (6-8), it is seen that the process depends on the formation of Mg^{++} and OH^- ions and subsequent neutralization of sulfurous acid. The formation of Mg^{++} and OH^- ions, however, is dependent upon the hydration

*See Section 11, References.

characteristics of solid MgO. A recent paper (2) on the hydration of MgO has shown that the rate controlling step is the removal of solid $\text{Mg}(\text{OH})_2$ particles from the surface of the solid MgO. In agreement (3) with the above, both MgO and $\text{Mg}(\text{OH})_2$ of similar surface area have been shown to react at the same rate with aqueous CO_2 .

The above conclusion is only valid, however, when the MgO is in a reasonably active form. The other factor which affects the process is the particle size of MgO. Not only do the finer particles react faster, but also being smaller, they remain suspended for longer periods of time and thus have a better chance to react with SO_2 .

6.1.1 Pulverization

Early attempts to use calcined magnesia in the absorption system without any intermediate processing were unsuccessful. The product MgO, as it exited the kiln coolers, was gritty and contained a small percentage of agglomerates. When this material was added as a slurry, it settled rapidly with the result that the MgO slurry pumps and lines plugged. Finally the lack of a fine dispersion of magnesia caused further problems with pH control.

A small, high speed hammermill (Micro Pulverizer 2DH) was installed first at Boston and, after a brief trial period, was moved to the regeneration facility where it was installed to pulverize the calciner product.

Several varieties of screens and hammers were tried in this unit and two of the screen types were moderately successful in producing a satisfactory pulverized product. There were herringbone pattern screens and jump gap screens. Neither type had a satisfactory service life as would be expected with the abrasive regenerated magnesia.

Herringbone pattern screens had a service life of 4 to 8 hours. The jump gap screens gave better service as did hard faced hammers and lined head plates. Average replacement times are as follows:

Jump Gap Screens	185 hours
Hammers	1500 hours
Head Plates	230 hours

Table 18 shows the size distribution before and after pulverization of the regenerated magnesia as well as the distribution of the unpulverized calciner product.

6.1.2 Hydration of MgO

Digestion of MgO in water resulted in slaking of the MgO and formation of $\text{Mg}(\text{OH})_2$ which subsequently reacts with SO_2 . The conditions necessary for efficient slaking of regenerated MgO were investigated in the laboratory using the SO_2 utilization test (Appendix C) developed to monitor calciner operation. The effect of digestion temperature using this same test is given in Table 19, while the rate of hydration for various samples treated at 180°F in water given in Table 20.

6.2 SYSTEM pH AND SO_2 ABSORPTION

From equations (6-5) and (6-6) it is seen that the formation of solid MgSO_3 is dependent on the pH of the absorbing system. It is also evident from the pK values of H_2SO_3 , Table 21, that sulfurous acid (considering the SO_3^{-2} ion) is a weaker acid than acetic acid.

Coupled with this is the fact that alkaline-earth sulfites dissolve readily (4) in moderately strong acids (even in sulfurous acid). Thus pH values near 7 were selected for operation.

Because of the weakly acidic character of sulfurous acid, the salts, especially alkali and alkaline-earths, are hydrolyzed in solution and consequently the sulfites are alkaline in nature.

Titration of SO_2 in water by MgO and $\text{Mg}(\text{OH})_2$ suspensions support the above conclusion, i.e., for more than 90% removal the pH of the final suspension should be above 7.

TABLE 18
 DRY SCREEN ANALYSIS

Screen Size (Tyler)	Unpulverized Calciner Product A	Pulverized Calciner Product	
		Herring Bone Screen B	Jump Gap Screen C
+50	30.3		5.3
+100	18.1	39.1	9.5
+200	9.4	9.4	8.8
+325	13.1	3.3	49.8
-325	29.1	48.2	26.6

TABLE 19
EFFECT OF TEMPERATURE OF DIGESTION OF MgO
ON SO₂ REMOVAL CAPACITY

Sample	Treatment	SO ₂ Efficiency
Al ₂ O ₃ , 97.4% B/D 46.40#/ft. ³	a. Untreated.	20
	b. Digested at 160°F for 45 mins.	50
	c. Digested at 180°F for 45 mins.	72
MgO, 97.35% MgSO ₄ , 0.50 B/D 68#/ft. ³	a. Untreated	22
	b. Digested at 180°F for 1/2 hr.	42
	c. Digested at 180°F for 1 hr.	49
	d. Digested at 210°F for 1/2 hr.	45

TABLE 20

RATE OF HYDRATION OF MgO at 180°F. in WATER: 10% SLURRY

Time in Minutes	MgO (AR)			R-1616			R-1310		
	% MgO after Hydration	% of Hydration	% MgO after Hydration	% MgO after Hydration	% of Hydration	% MgO after Hydration	% MgO after Hydration	% of Hydration	% of Hydration
15	79.50	48.20	71.79	53.35	90.61	90.00	0.00		
30	74.82	64.27	67.18	68.20	90.00	90.00	1.96		
45	72.32	71.32	66.36	70.81	89.34	89.34	4.09		
60	70.96	75.70	65.68	73.03	89.08	89.08	4.93		
90	69.36	80.85	64.47	76.92	88.51	88.51	6.76		
120	68.65	83.14	64.45	76.99	86.55	86.55	13.07		

TABLE 21

	<u>Ka</u>	<u>pKa</u>
$\text{H}_2\text{SO}_3 \longrightarrow \text{H}^+ + \text{HSO}_3^-$	1.54×10^{-2}	1.82
$\text{HSO}_3^- \longrightarrow \text{H}^+ + \text{SO}_3^{-2}$	1.02×10^{-7}	6.91

For comparison the pK values of other acids are:

$\text{H}_2\text{CO}_3 \longrightarrow \text{H}^+ + \text{HCO}_3^-$	<u>pKa</u> 6.37
$\text{HCO}_3^- \longrightarrow \text{H}^+ + \text{CO}_3^{-2}$	10.25
Acetic Acid	4.75

6.2.1 SO₂ Absorption

The absorption of gas in a venturi device follows conventional mass transfer principles. In the venturi absorber used in this work, flue gas containing SO₂ enters the converging section of the vessel and is accelerated towards the throat area, passing over surfaces which are irrigated by the absorbant slurry. The moving gas creates a wave motion on the liquid surface until, at a critical velocity, the forces resulting from the frequency and amplitude of the waves exceeds the cohesive (surface tension, etc.) forces of the liquid, When this occurs, some portion of the wave is detached and dispersed into the gas stream.

The liquid, dispersed as droplets into the gas stream, provides the media for absorption. The equation for point efficiency,

$$(1-E) = \frac{P_{SO_2f} - P_e}{P_{SO_2i} - P_e} = \exp \left[\frac{-K_g a Z}{G} \right] \quad (6-16)$$

where (E = Efficiency
(P = Partial Pressure of the Absorbed Gas
(K_g = Overall Mass Transfer Coefficient
lb mole/hr. ft.²
(Z = Axial distance, ft.
(G = Mass Velocity, lb mole/hr.ft.²
(a = Area, ft²

was used in deriving relations for removal efficiency.

The surface area can be determined from the liquid to gas ratio in the absorber and the mean liquid drop size.

$$S = \frac{3.05 \times 10^5}{D_o} \frac{V_l}{V_g}$$

where S = Specific Surface Area, ft.²/ft.³ (6-17)

V_l = Volume of liquid, ft.³

V_g = Volume of gas, ft.³

D_o = Mean drop diameter, microns.

An estimate of D_o can be obtained from the Nukiyama and Tanasawa equation.

$$D_o = \frac{585}{U_g} \sqrt{\frac{\sigma}{\rho}} + 597 \left(\frac{\mu}{\sqrt{\rho}} \right)^{0.45} \left(1000 \frac{v_l}{V_g} \right)^{1.5} \quad (6-18)$$

where U_g = Velocity of the gas, meters/sec.

ρ = Liquid density, gm/cc

μ = Liquid viscosity, poise

σ = Liquid surface tension, dynes/cm

For cases where gas phase resistance is controlling an analogous form of equation (6-16) based on system pressure drop has been used (5) to correlate data as ΔP is a function of gas flow and thus dispersed area. In this form

$$1 - E = \exp \left[-A \Delta P^B \right] \quad (6-19)$$

where ΔP = differential pressure (in H_2O)

A&B are constants

For other cases other than gas film controlling an over-all mass transfer co-efficient is defined as:

$$\frac{1}{K_{ga}} = \frac{1}{k_{ga}} + \frac{n}{k_{la}} + \frac{n}{k_{sa}} + \frac{n}{k_{ra}} \quad (6-20)$$

where n = Henry's Law constant ($lb \text{ mol}/ft.^3$)

(Subscripts refer to the gas film, liquid film, solubility, and reaction resistances respectively.)

As the chemical reactions involved in the absorption are acid-base (fast) reactions, the final term in (6-20) is zero. Recent investigations (1) have also determined that the solids dissolution resistance is zero, and that the liquid phase and gas phase resistances are each approximately one-half of the total. To incorporate the contribution of liquid film resistance, we have correlated the data in

the form

$$1 - E = \exp \left[\frac{-A \Delta P^B}{(10^{pH})^C (SO_2)^D} \right] \quad (6-21)$$

where the denominator in (6-21) represents the liquid film resistance. This correlation is shown graphically in Figure 29, which presents the results obtained using the final form of the prediction equation:

$$1 - E = \exp \left[\frac{2.666 (\Delta P)^{-1.014}}{(SO_{2I})^{3.75 - 0.271 \ln SO_{2I} (10)^{-6 + 0.031 pH}} \right]^{-3} \quad (6-22)$$

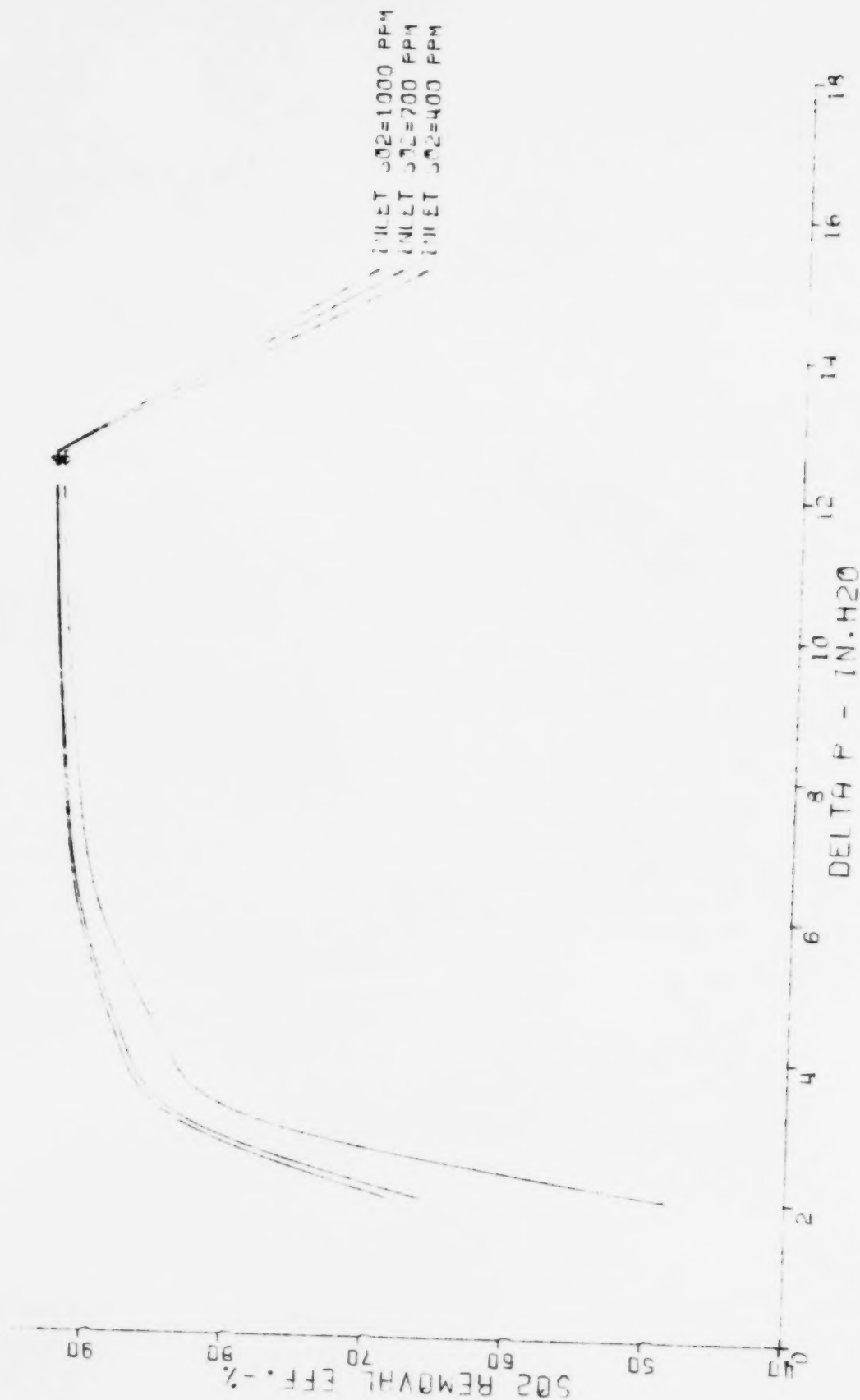
E = Fraction SO₂ Removal

ΔP = Pressure Drop, Inches H₂O

SO_{2I} = Inlet Concentration SO₂, PPM

This prediction equation was developed from both the data obtained during the operations at Mystic Station in Boston, and from some subsequent additional data obtained during initial operations at an installation on a coal fired boiler. This latter operation provided data for extension of the equation to higher pressure drops.

The correlation also illustrates the relatively small change in SO₂ removal efficiency over wide turn down ratios of the power generator. The high efficiency of SO₂ removal over the ranges of power output of a cycling generating station is explained by the relative invariance of the surface area available for mass transfer over that range. Figure 30 is a plot of surface area, based on uniform drop size, for a constant liquid rate, which shows only a 33% reduction in surface area for a 4 to 1 turn down, equivalent to operations between 40 MW and 150 MW Mystic #6 power generator.



SO₂ REMOVAL EFFICIENCY
EFFECT OF DELTA P AND INLET SO₂ CONCL.

FIG. 29

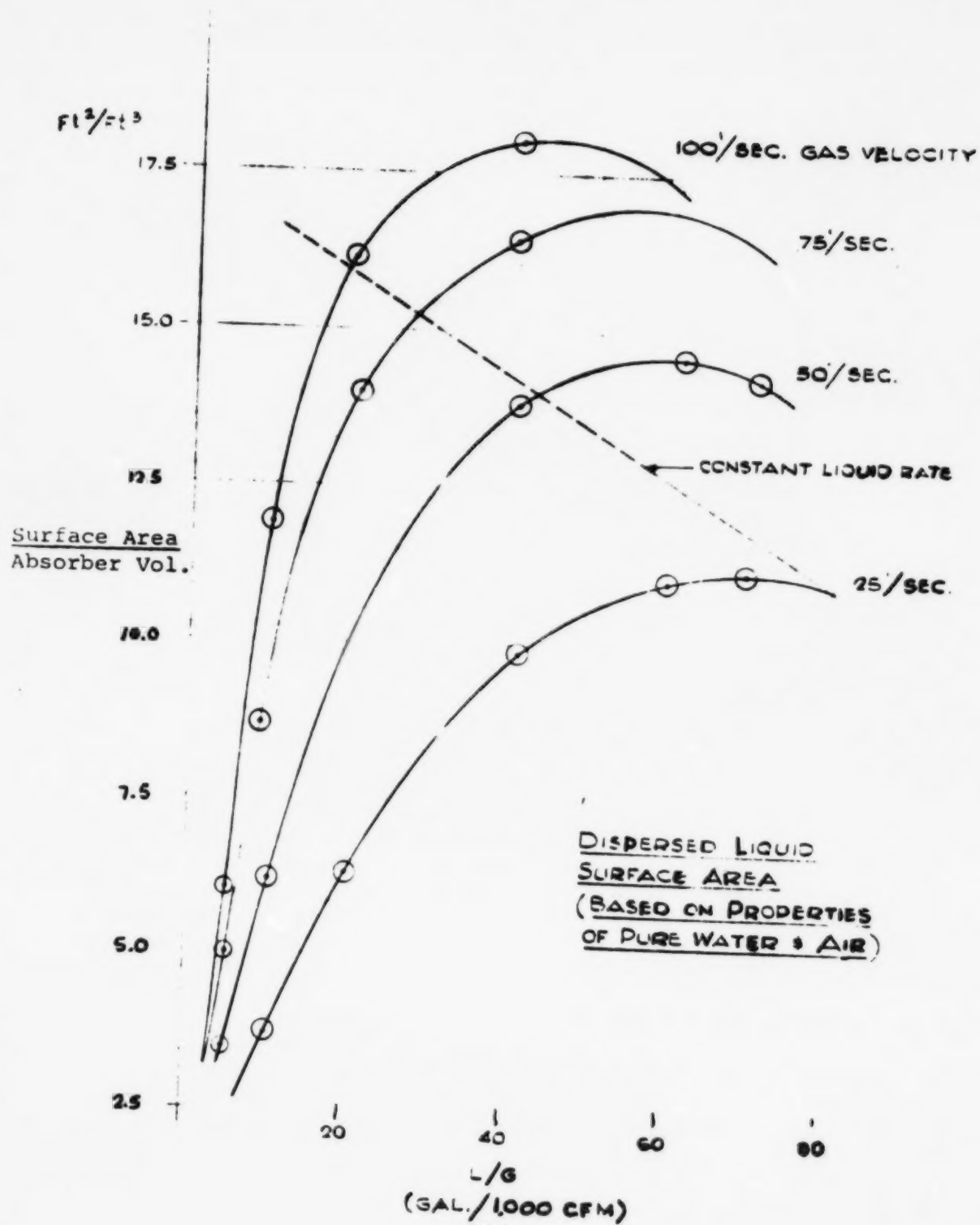


FIG 30

An estimate of the accuracy of the correlation in predicting SO₂ removal efficiency is given below:

ACCURACY OF SO₂ REMOVAL CORRELATION

<u>Source of Data</u>	<u>No. of Points</u>	<u>Standard Deviation</u>
Boston Edison	600	4.0
Coal Fired Boiler	5	2.9
Boston Test Runs Used to Check Correlation	5	3.1

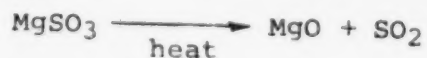
6.3 CENTRIFUGATION AND SOLIDS SEPARATION

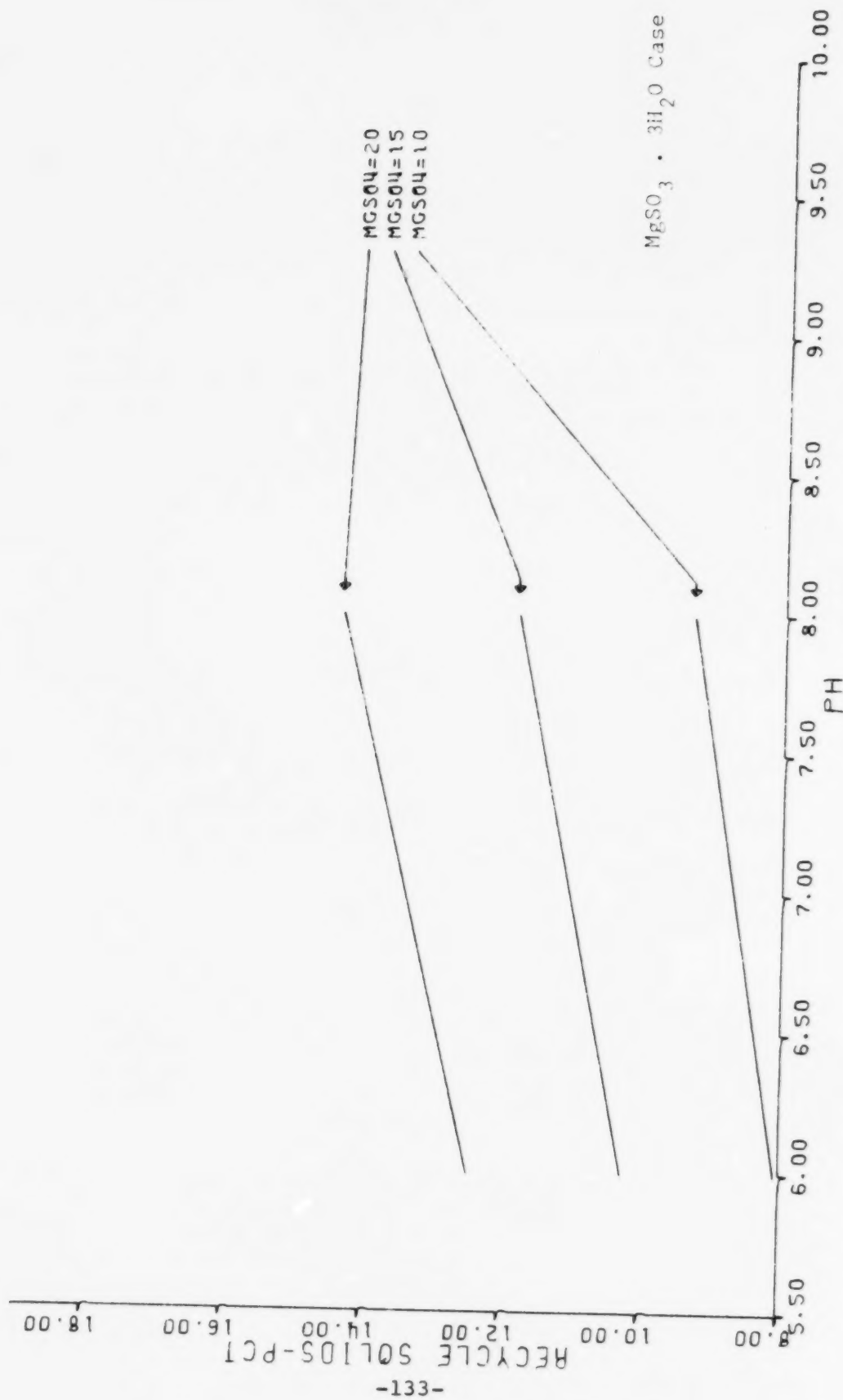
The centrifuge was normally capable of separating 50% of the incoming solids in the recycle slurry, but some instances were encountered in which the centrifuge did not perform satisfactorily, i.e., solids were not removed at a rate sufficient to maintain control of recycle solids concentration.

In all, during the entire program, operations were interrupted three times by inability to control slurry solids by centrifuging the bleed stream. An analysis of the conditions prevailing showed that during these periods magnesium sulfate level was higher than normal in the recycle liquor, an effect which arose because of changes in operating conditions. In addition, the concentration of MgO in the slurry was also shown to have an effect. These relations are shown in Figure 31 which relates recycle solids concentration to MgSO₄ level and pH.

6.4 REGENERATION MECHANISMS

The principal operation in the regeneration plant is the calcination of the dryer product from the absorption system. This can be most simply described as a thermal decomposition:

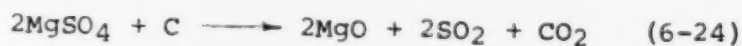




EFFECT OF SYSTEM PH AND MGSO₄ LEVEL
ON RECY. SOLIDS CONTENT -DATA TO 3/12/74

The rate of the decomposition is temperature dependent, and some decomposition has been observed at temperatures as low as 300°C. For the production of useful product in this program, the rotary calciner has been operated at mid kiln temperatures above 1000°F.

In addition to the simple decomposition of MgSO_3 , the calcination step also serves the purpose of reducing the MgSO_4 , a side product in the absorption reaction which is also present in the feed. This reaction can be represented by either of the following equations:

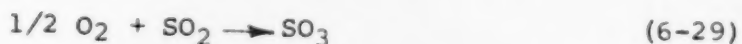
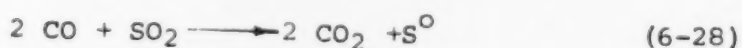
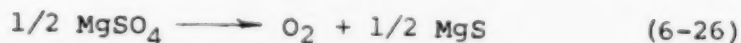


$$\Delta G \text{ } 1100^\circ\text{F} = -31\text{KCal}$$



$$\Delta G \text{ } 1100^\circ\text{F} = -14 \text{ KCal}$$

Other reactions can also take place in the kiln environment:



All of these reactions are both time and temperature dependent and the calciner is equivalent to a multi-zone linear reactor. In the course of the program, in addition to the production of thousands of tons of acceptable regenerated MgO , upset conditions have occasionally resulted in the formation of high concentrations of SO_3 and at other times in the formation of elemental sulfur.

Attempts have been made to study these upset conditions in the laboratory, and thermal decomposition studies have been carried out on a laboratory scale using infrared spectroscopic techniques to investigate the phenomenon of sulfur

formation by detection of the appearance of its precursors. Those studies, which are described more fully in Section 6.1, have not as yet yielded any specific information on the formation of elemental sulfur; however, they have yielded information indicating that the decomposition process for MgSO_3 obtained from the trihydrate form and the hexahydrate form may be different.

Retention time in the calciner can be determined from the following equation:

$$\theta = \frac{0.19 L}{N D S}$$

where θ = time (min.)
L = kiln length (ft.)
N = Rotational Speed (RPM)
D = Dryer Diameter (ft.)
S = Slope (ft./ft.)

For most operations undertaken during this project retention time was approximately one hour. Because of the use of tube coolers on the calciner, an additional one hour was required before final discharge to the product conveyors.

Studies of heat transfer in a rotary kiln (8) have resulted in the formulation of prediction equations for the solids - gas temperature relations considering the following:

- 1) Gas to solid heat transfer.
- 2) Gas to calciner wall heat transfer.
- 3) Calciner wall to solid heat transfer.
- 4) Conduction thru the kiln wall.
- 5) Conduction and convection to ambient air from the kiln.

Such studies have not considered the additional complications of chemical reaction in the charge or radiation from the flame at the discharge end.

The data resulting from the test program phase of this project were analyzed to provide correlations for both the percent of MgSO_4 in the product and the bulk density of the product. These correlations are given in the following equations 6-31 and 6-32, and provide a means of determining the processing condition necessary for the production of an active magnesia and control of magnesium sulfate concentration.

CALCINER OPERATIONS
CORRELATION FOR PREDICTION AND CONTROL
OF % MgSO₄ IN REGENERATED MAGNESIA

$$\begin{aligned} \% \text{MgSO}_4 = & -90.2 + (T' \cdot A) + (C \cdot B) - 2.46 (\% \text{MgSO}_4 \text{ in feed}) + 0.989 (\% \text{MgSO}_3 \text{ in Feed}) \\ & + 4.1 (\% \text{O}_2 \text{ in Acid Gas}) + 0.28 (\text{Feed Rate, Lb./Min}) \end{aligned} \quad (6-31)$$

Where $T' = (1700 - ^\circ\text{F Mid Kiln Temperature})^{1/2}$
 $A = -0.870 + 0.185 (\% \text{MgSO}_4 \text{ in Feed})$
 $B = 15.7 - 23.4 (\text{Furnace Draft}) - 2.19 (\% \text{O}_2 \text{ in Acid Gas})$
 $\quad - 0.61 (\% \text{MgSO}_4 \text{ in Feed})$
 $C = \% \text{Carbon in Feed}$

Statistics: Standard Deviation = 5.4
 Multiple Correlation Coefficient = 0.77
 Confidence Level of F Ratio = 99.9% +
 No. of Data Points = 207

CALCINER OPERATIONS
CORRELATION FOR PREDICTION AND CONTROL
OF BULK DENSITY OF REGENERATED MAGNESIA

$$BD = 169.2 + (T' \cdot A) + (C \cdot B) + 0.741 (\% \text{ MgSO}_4 \text{ in Feed}) - 0.744 (\% \text{ MgSO}_3 \text{ in Feed}) - 4.9 (\% \text{ O}_2 \text{ in Acid Gas}) - 0.4 (\text{Feed Rate, LB./MIN.}) - 104 (\text{Furnace Draft}) \quad (6-32)$$

Where $T' = (1700 - ^\circ\text{F Mid Kiln Temperature})^{1/2}$

$A = -0.891 + 0.166 (C)$

$B = -28.4 + 3.44 (C) + 71.2 (\text{Furnace Draft}) + 1.95 (\% \text{ O}_2 \text{ in Acid Gas}) - 1.24 (\% \text{ MgSO}_4 \text{ in Feed})$

$C = \% \text{ Carbon in Feed}$

$BD = \text{Product Bulk Density, LB./FT.}^3 \text{ (Operations @ 1.82 RPM)}$

Add 5 to BD for 1.56 RPM)

Statistics: Standard Deviation = 7.2

Multiple Correlation Coefficient = 0.79

Confidence Level of F Ratio = 99.9% +

No. of Data Points = 456

6.4.1. Magnesium Sulfate Control

It has been shown (6-14, 6-15) that magnesium sulfate formation occurs to some extent in the process due to both the presence of oxygen and SO_3 in the flue gas entering the venturi and some additional conversion of MgSO_3 to MgSO_4 in the dryer.

It is necessary to reduce and control the magnesium sulfate concentration in the recycled MgO in order to prevent both: ultimate conversion of the absorbent to the sulfate and to prevent centrifugal separational problems associated with the increasing viscosity of more concentrated MgSO_4 solutions.

Direct reduction of magnesium sulfate in the calciner by operation at temperatures sufficient to thermally decompose MgSO_4 (2000°F) would cause "dead burning" of the magnesia product and render it useless for absorption of SO_2 . It is evident from 6-24 and 6-25 that the presence of carbon in the calciner feed can result in the reduction of the MgSO_4 contained in it at temperatures which still produce a useful product.

At the outset of the program carbon, in the form of coke, was added to the process. However, difficulty in obtaining a grade of coke sufficiently low in ash prevented a controlled program of carbon addition. After the initial operations of the F.G.D. System it was noted that the incoming calciner feed contained some carbon which had been removed in the venturi as uncombusted fuel or "oil smut" from the flue gas. A number of analyses of the calciner feed revealed that the feed had an average carbon content between 0.5% and 1% which was sufficient for control of the magnesium sulfate in the product. Normally, the calciner was operated to reduce the MgSO_4 content from 11% in the feed to 5% to 8% in the products, i.e., reduction of 50% to 70% of the incoming sulfate.

Equation 6-31 provides the empirical relationship between the control variables and the MgSO_4 content in the regenerated product. This is presented graphically in Figure 32.



CALCINER OPERATION - EFFECT OF
MIDKILN TEMP. & %C ON %MgSO₄ IN PRODUCT
Fig. 32

6.4.2 Magnesia Activity Control

The principal control parameter in the calciner operation has been the bulk density of the regenerated MgO. Values of calciner product bulk density between 20 and 25 lb/ft³ have resulted in better performance in the F.G.D. System, and the property can be readily measured by the calciner operator using several commercially available devices. In this work a "paint pigment volumeter" was used.

The effect of carbon content and mid-kiln temperature on the product bulk density, developed from equation 6-32, has been shown in Figure 1.

6.5 MgO LOSSES AND REGENERATION CYCLES

A) Losses

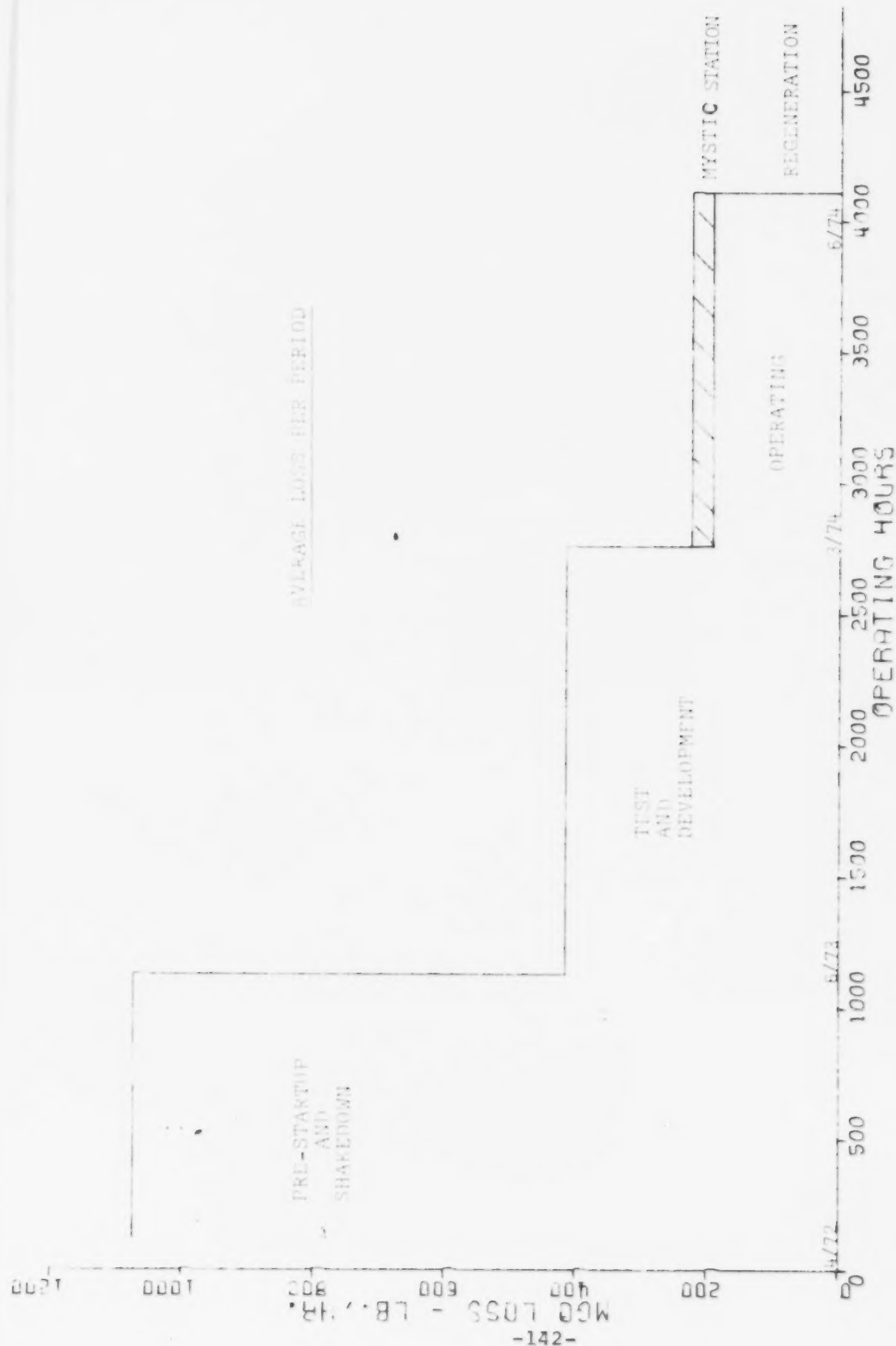
In early operation of the system, losses of MgO were high. The main losses resulted from: frequent clean out of plugged equipment, discarding both oversize materials and any spilled solids, entrainment to the stack, overflows, and cleaning the absorber when the system was shut down.

By June 1973, the installation of lump crushers and re-routing the dryer off gas to the absorber, reduced the loss substantially but did not eliminate it. Spills were still discarded and the venturi absorber was still drained on shut down. Another continuing contributor to the loss of alkali was the higher than design gas flow, which resulted in excessive entrainment of absorber slurry.

In the final period of operation, from March 1974, controls were imposed to eliminate many of the loss points. During part of this period a careful measurement of system losses were made in order to identify the sources which could not be eliminated in the current program for future design improvements.

The loss history for the entire operating period is accounted for on a rate basis in Figure 33.

In the initial operations, startup and shakedown, system losses averaged 1075 lb/hr. of operation or a total



PROCESS MGQ CONSUMPTION
BY OPERATING PERIODS

Fig. 33

of 606 tons as MgO in the 1127 hours logged from initial startup in April 1972 to the completion of the first phase in June 1973.

The second period, the test and development program, had an average MgO loss rate of 415 lb/hr. of operation. The total loss in the 1350 hours logged from July 1973 to February 1974 for this phase of operations was 151 tons as MgO.

Similarly, in the final period from March to the end of the program, losses averaged 234 lb/hr. as MgO; a total of 151 tons of MgO lost in 1293 hours logged.

A comparison of the measured losses at Mystic Station (cross hatched) and the losses from the regeneration plant for the March through June 1974 period are also shown in this figure. It should be noted that the regeneration plant losses were approximately constant during the entire program.

In the final operating period at Mystic Station, gas flow to the absorber was maintained at the design rate and the system was run as a closed loop with no vessel drainage, returning the small spills back to the process. Measurements were made at the following 14 loss points (Table 22) at Boston for the continuous operations period and the silos were emptied and the contents weighed before and after the run for accuracy of inventory measurements.

Table 22
Potential Sources of MgO Losses at Mystic Station

- 1) Stack
- 2) Centrifuge Washing
- 3) Centrifuge Case Leaks
- 4) Pump Packing Gland Leaks
- 5) Absorber Overflow
- 6) MgO Slurry Tank Blow-Down
- 7) MgO Slurry Tank Overflow
- 8) Centrate Tank Overflow
- 9) Solids Loss at Dryer Feed End
- 10) Dust Loss at Dryer I.D. Fan
- 11) Dust Loss at Expansion Joints

- 12) Spillage at MgO Feeder
- 13) Spillage in MgSO_3 Belt Gallery
- 14) Spillage at Truck Loading Point

The tests, conducted over 13 days, in which 336,470 lbs. of regenerated material were fed (an additional 2,504 lbs. of MgO added with the fuel oil was also accounted for), showed a loss of 0.37 tons/operating day at the absorber system, distributed as follows:

	<u>Ton/Day</u>
Loss to Stack	0.13
Absorber Overflow	0.14
Misc. Measured Loss	0.07
Unmeasured Loss (by difference)	<u>0.03</u>
	0.37

With an average MgO consumption in the process of 10.61 tons/day during the period, the 0.37 tons/day loss represents a 3.5% loss rate at the F.G.D. System.

The greatest losses were found however, to occur at the regeneration plant. Here 1.5 tons/day of equivalent MgO is lost from the neutralizer system overflow and another 0.5 tons per day is scalped off, for future reclamation, before being pulverized.

Both of these losses would be virtually eliminated in a full size regeneration plant.

B) Regeneration Cycles

The information on total losses has been combined with the other inventory records including the receiving records for virgin MgO shipments to evaluate the number of regenerations. In the start-up and shake-down period, losses were 606 tons of MgO, with 559 tons of regenerated MgO recycled to the Mystic #6 System. This rate of loss limited the number of recycles from 2 to 3 before the material was lost from the system.

During the test and development period, 1717 tons of regenerated MgO were returned to the system, while 338 tons of MgO equivalent were lost. This corresponds to 5.1 cycles for the magnesia before it is lost from the system.

During the final period, 151 tons of magnesia were lost, while 875 tons of regenerated alkali was shipped back to Boston. This would correspond to 5.8 cycles; however, during this same period there was an inventory build-up with 80 tons of equivalent MgO inventory at the beginning, and 214 tons remaining at the close of the program so that only five regeneration cycles can be accounted for.

7.0 DESCRIPTION OF THE TEST AND DEVELOPMENT PROGRAM

A test program was developed for the "New England SO₂ Control Project" on the basis of two years operation of the system.

This planned program was divided into three phases, first a period of start-up and break in operations of the integrated plants carried out over a three to six months period. Then a twelve month period in which several variables, considered to be most important for successful operation of the system, were to be investigated by operating the plant setting the variables to evaluate performance and determine the best methods of overall system control. A final period of three to six months of operation at optimized conditions was planned to demonstrate the long term capability of the project and provide further information on the results of continuous "on stream" running.

The actual operating periods for the Start-Up and Break-In Tests and the Variables Screening Tests deviated considerably from the proposed plan to conform to the situations which are described in the previous sections. A further complication to controlled operation arose because of the economic-dispatch method of setting boiler load which favored maximum load on the Mystic 6 unit when it was fired with high sulfur fuel. For this reason, the F.G.D. system treated a higher than average gas flow based on the load data supplied by Boston Edison Company. Except for disruption of any test plan, the effect on operation was not serious as the F.G.D. System had been designed for continuous full load operation although complications were introduced by the greater than design gas flow.

It was not till the last six months of the program, after approval was obtained from local authorities for a partial gas bypass, that the F.G.D. System could be operated at its design gas flow while the boiler was fired at its maximum rating.

7.1 TEST PROGRAM

While the time schedule of the program was changed, the goals of the three periods remained the same and the test plan is summarized to show the scope of the project.

7.1.1 Start-Up and Break-In Tests

An initial period of testing started after mechanical completion of the plant had been accomplished. A prestart period was included which was limited to the accumulation of 2 days production of MgSO_3 at the Boston Edison site.

This initial period was to demonstrate the operability of all equipment at Boston Edison as well as the integrity of the piping and equipment. After pre-start-up, the start-up and break-in period continued under Chemico supervision and shipment of MgSO_3 to the calcining facility was initiated to begin integrated operation at both sites.

During this period operating, testing and analytical procedures were tried and evaluated; equipment tested, and additional training completed. In addition, the first phase of testing started in order to find the conditions necessary to achieve even a limited level of system operability.

This initial period provided wide ranging operating conditions as flows and equipment settings were adjusted to and modifications made to obtain a satisfactory level of semi-continuous performance of the recovery-regeneration facilities. All data collected during this period were accumulated for use in the statistical analysis programs used to assess the program.

7.1.2 Variables Screening Tests

Following the Start-up and Shake-down period, a test and development program, designed to investigate the effects of primary process variables on the overall operation was initiated. After determining conditions which made the plants functional during the first period, certain process variables were chosen for study and the effect on plant operation gauged.

The program was to establish a model of the principal process mechanisms from which the effect of changes in operating conditions could be evaluated. From this model (and consideration of pilot plant results), preliminary values for the parameter excursions were chosen, and experimental sets planned so that the data collected could be used for optimization of the process. After initial tests to evaluate the effect of the variable excursions, and to determine if modifications to the scheme are necessary, further optimization followed an evolutionary plan in order to minimize system upset. That is, the range allowed to the parameters under examination were regulated in order to insure minimum system upset and negligible effect on power plant operation.

Information was collected at these operating conditions for a sufficient length of time to insure that the effects could be determined with sufficient reliability by the use of statistical methods. Other variables or combinations of variables were then selected and the process repeated to provide information for the data file in order to establish regression equations to determine variable effects and interactions at levels not specifically tested.

7.1.3 Long Term Tests

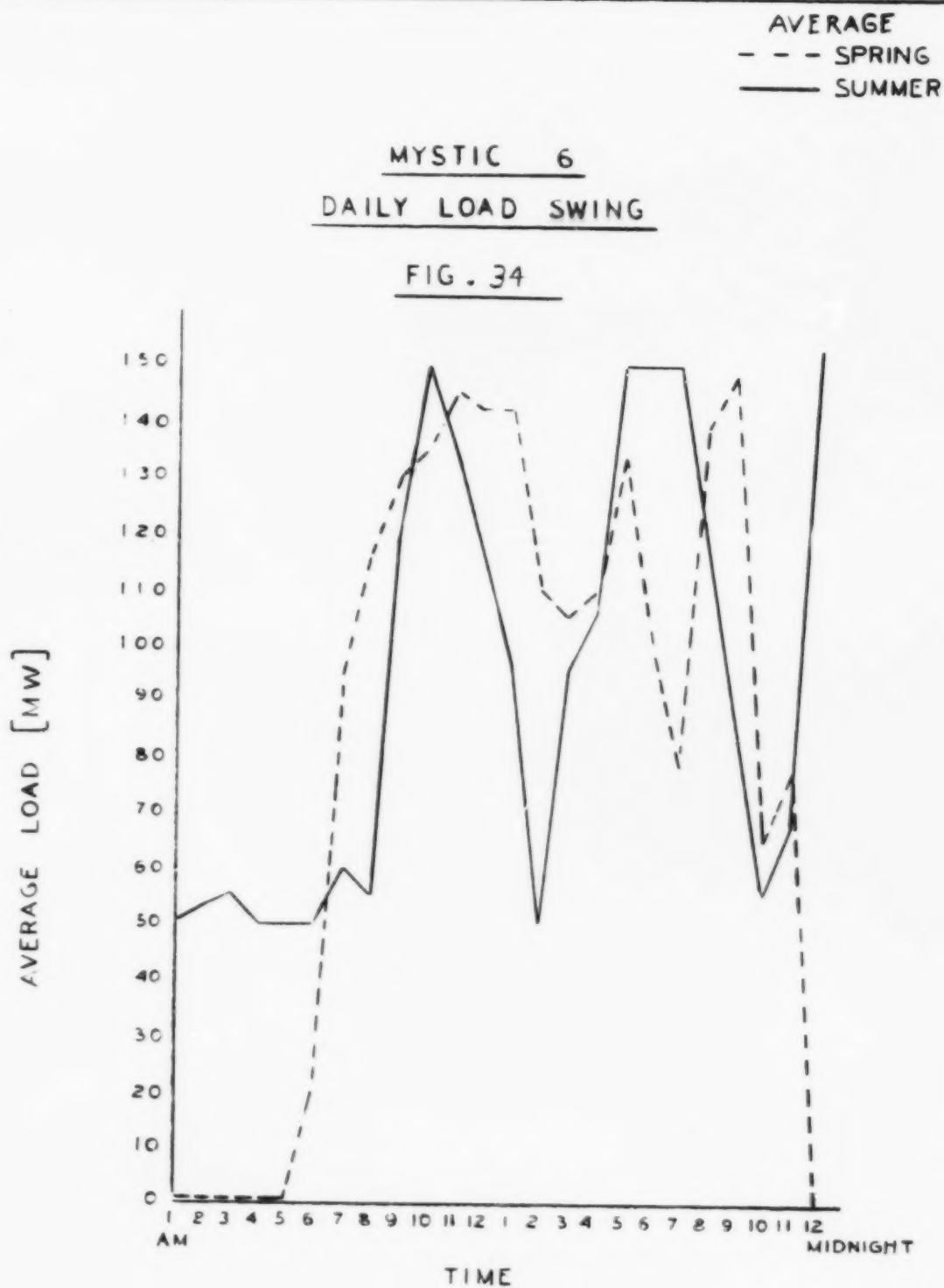
During the design of the variables screening portion of the Operational Tests Program the assumption of careful control of all variables was assumed. For any test the boiler load was to be held within specified narrow limits for the test period in order to evaluate the performance of the associated flue gas scrubbing equipment under the controlled conditions. The long term tests were to follow the normal operating ranges of the power boiler. Figure 34 shows seasonal load variation based on data supplied by Boston Edison Company and Figure 35 shows average daily load swings for both spring and summer operation. By following the load swings the effect on F.G.D. System operation could be determined.

7.2 STATISTICAL METHODS

Throughout the term of operation of the program, large amounts of process data were generated. In order to effi-

MYSTIC 6
DAILY LOAD SWING

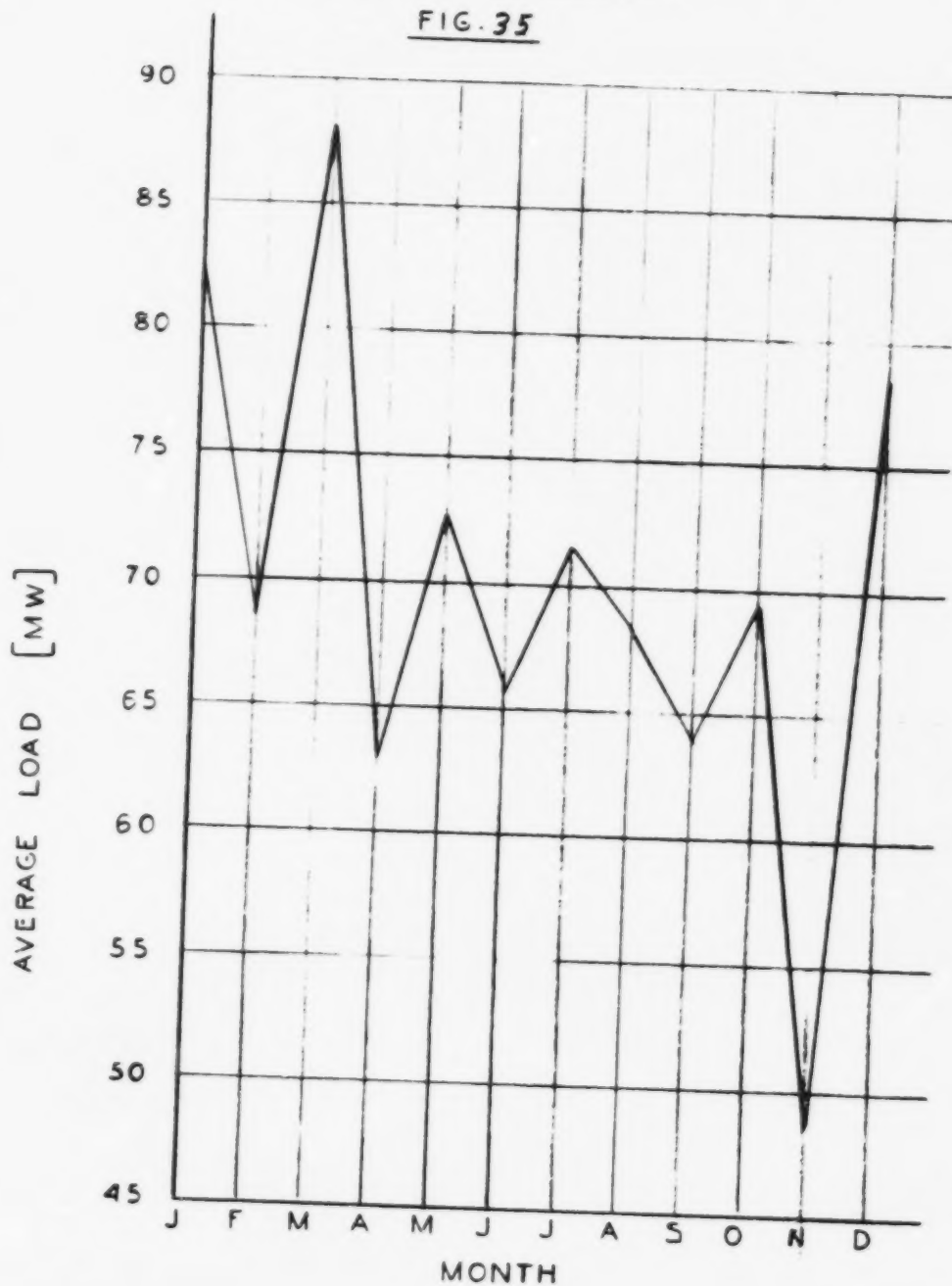
FIG. 34



MYSTIC 6

SEASONAL LOAD SWING

FIG. 35



ciently assimilate, disseminate, analyze, and store this information, a computerized, statistical method of handling the data was employed. As a result, it was possible to effect a real-time feedback to the process of correlated and trend results at the time they would be most useful, along with accumulating a permanent data bank available for analysis and retrieval. The statistical computer program package utilized permitted the use of the same format data file as input to a wide range of sub-programs, including regression calculations, x-y plotting, file listings, trend plots, etc. This flexibility reduced the number of files which needed to be maintained, in addition to the evident speed advantages.

Figure 36 illustrates the flow of information between both the scrubber and calciner operating systems and the computer data bank. Operating conditions and analyses were entered on punch cards on a daily basis for primary storage and transferred to computer disk files for further processing. At monthly intervals the following statistics were generated for all variables: average, maximum, minimum, standard deviation, and a percent change relative to a base period. The final stage in the data flow was the integration of the operating log and analysis files, plus the inclusion of appropriate time lags for the scrubber and regeneration facilities to form single disk files suitable for input to correlation and plotter computer programs. This process data bank is now a source of rapid retrieval of process information for continued analysis and for comparison with results from other installations.

The process correlations presented in previous sections were developed primarily using the data bank as input to a stepwise multiple linear regression program. This approach minimizes the number of computer runs required to determine equations which are statistically significant, and which have been evaluated for consistency with observed data. F ratio tests are employed to establish significance levels for testing of equation variables, and coefficients are calculated by least squares techniques. With respect to the SO₂ removal efficiency correlation, log transformations were required by the regression program. Continued investigation of mass transfer coefficients may lead to the use of non-linear programs.

PROCESS DATA FLOW DIAGRAM

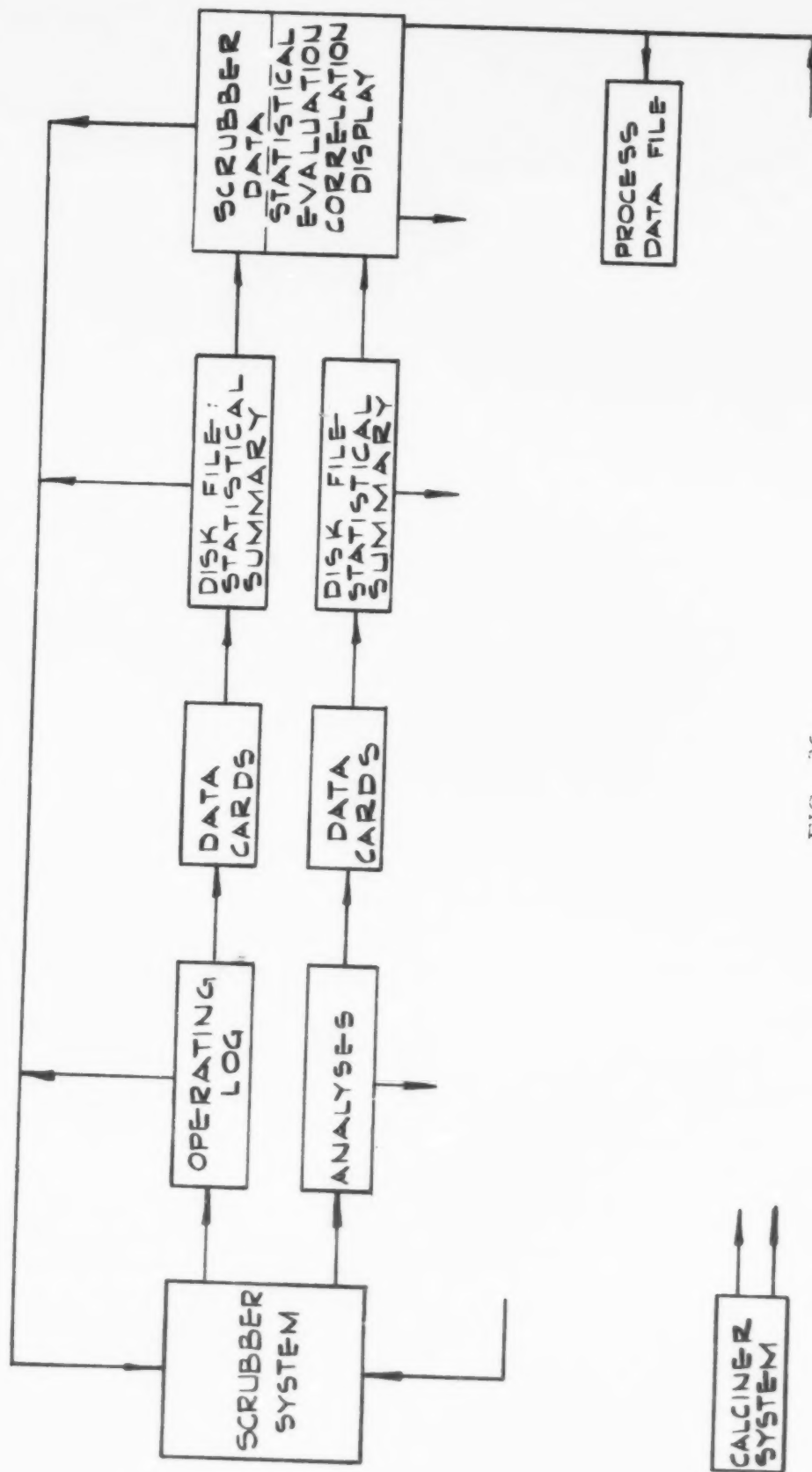


FIG. 36

CALCINER
SYSTEM

As discussed in Section 7.0, Description of the Test and Development Program, normal excursions in the process variables were sufficient to satisfy the required scope of the test program variation in levels of operating data.

8.0 PERFORMANCE TEST RESULTS

Performance tests on the Chemico Basic Magnesia System installed at the Mystic Station were conducted by York Research Corporation for Boston Edison Company. The testing period extended from February 27, 1974 through March 9, 1974 following a preliminary period in early February for equipment set-up, familiarization, establishing gas velocity profiles and gas flow measurement.

The performance testing used the methods detailed in the Federal Register, Vol. 36, No. 247, 1971 for:

- a) Gas analyses by Method 3
- b) Particulate removal efficiency by Method 5
- c) SO₂ removal efficiency by Method 6

In addition, particulate removal efficiency for a range of particle sizes was done using the method developed by J. A. Brink (9). The results are presented for SO₂ removal efficiency in Table 23, for overall particulate removal efficiency in Table 24, and for particle size removal efficiency in Table 25. Oil analyses data for the test period are presented in Table 26. These data has been abstracted from the York Research Corporation's report No. Y-8419 dated April 11, 1974.

TABLE 23

SO₂ REMOVAL - TEST RESULTS

TEST NO.	BOILER LOAD: MW	INLET GAS RATE: ACFM	SO ₂ IN PPM - VOL.	SO ₂ OUT PPM - VOL.	% SO ₂ REMOVAL	SO ₂ OUT LB/100 BTU
1	146 ¹	446,953	926.1	71.1	92.3	0.125
2	144 ¹	486,991	1004.5	89.0	91.1	0.199
3	151 ²	658,207	983.9	63.3	93.6	0.201
4	148 ¹	503,233	833.3	86.6	89.6	0.243

- 1) Flue gas partially bypassed to stack to attain design gas flow.
 2) No flue gas bypass.

TABLE 24

PARTICULATE REMOVAL - TEST RESULTS

TEST NO.	BOILER LOAD: MW	INLET GAS RATE: ACFM	PARTICULATES: IN	PARTICULATES: OUT	REMOVAL	PARTICULATES LB/100 BTU
1	146 1	446,953	380	116	69.5	0.072
2	144 1	486,991	232	115	50.4	0.084
3	154 2	658,207	399	150	62.4	0.111
4	148 1	503,233	151	82	45.7	0.068

- 1) Flue gas partially bypassed to stack to attain design gas flow.
 2) No flue gas bypass.

TABLE 25
PARTICLE SIZE RESULTS

<u>Test No.</u>	<u>Removal Efficiency Above 1 Micron</u>	<u>Removal Efficiency Below 1 Micron</u>	<u>Overall Efficiency</u>
1	89.5	53.6	85.5
2	89.5	57.6	85.8
3	80.75	64.6	74.4
4	94.4	57.2	88.9

TABLE 26

OIL ANALYSIS

Parameter	Test #1 2/27/74	Test #2 2/28/74	Test #3 3/5/74	Test #4 3/9/74
BTU/lb	18,284	18,348	19,083	19,145
Specific Gravity	.9431 ^A	.9433 ^A	.9316 ^B	.9366 ^B
% Sulfur	2.15	2.10	1.89	2.04
% Ash	0.09	0.10	0.07	0.07
% Carbon	84.77	84.79	84.54	84.39
% Hydrogen	11.34	11.42	11.24	11.39
% Nitrogen	0.2	0.2	0.1	0.1
% Oxygen	1.45	1.39	2.16	2.01

A - Taken at 126°F, B - Taken at 130°F

9.0 DATA

9.1 OPERATING RESULTS

Operating data are summarized and presented as monthly averages for the period from the initiation of Planned Operational Testing through the end of the program. Included in this information are:

Table 27,	Operating Conditions for the FGD System
Table 28,	Stream Compositions for the FGD System
Table 29,	Operating Conditions for the Regeneration Unit
Table 30,	Stream Composition for the Regeneration Unit

9.2 RANGE OF SIGNIFICANT VARIABLES

Frequency distribution and the range of the important variables measured in this study are presented in Figures 37 through 63.

9.3 MISCELLANEOUS DATA

Table 31,	Sulfur Content of High Sulfur Oil for Mystic #6 Boiler
Table 32,	Oil Ash Analyses
Table 33,	Regenerated MgO Vanadium and Nickel Content

9.1

OPERATING RESULTS

TABLE 27
FLUE GAS DESULFURIZATION SYSTEM
OPERATING CONDITIONS

VARIABLE	MONTHLY DATA AVERAGES					
	5+6/73	7/73	8+9/73	10/73	11/73	12/73
SO ₂ (PPM)						
IN	603.01	789.45		734.45	741.80	594.83
OUT	78.65	106.50		86.53	107.31	91.05
%REMOV	87.07	86.24		87.03	84.24	83.89
PH	6.86	7.02	7.14	7.21	7.13	7.18
POWER PLANT RATE (MW)	132.02	127.26	116.59	123.62	106.16	124.02
DIFF. PRESSURES (IN. H ₂ O)						
TOTAL	9.79	10.05	9.01	9.02	7.25	9.30
WIST	4.89	5.06	2.63	2.49	1.40	0.92
DRYER	0.07	0.04	0.07	0.07	0.08	0.07
TEMPERATURES (°F)						
-ABSORBER						
INLETA	311.30	306.93	293.46	300.69	294.97	288.12
GAS OUT	113.87	116.73	117.43	121.37	124.08	120.98
SLURR.	123.60	128.00	123.01	124.41	123.25	131.96
MGSLUR	186.83	188.93	173.16	177.98	184.26	172.43
-DRYER						
GAS OUT	483.13	469.51	469.04	449.89	443.16	441.08
PROD.	295.06	315.77	350.02	339.82	332.13	340.68
FLOWS (GPM)						
CIRC.	14748.10	14458.67	13778.52	13484.79	12688.96	14185.61
CENTFD	118.62	110.57	102.91	114.12	128.27	120.60
MGSLUR	52.29	44.94	49.98	39.22	58.69	45.59
CENTRIFUGE TORQ. (GXS)	15.58	23.22	15.48	23.16	24.71	22.82

TABLE 27 (CONT'D)
FLUE GAS DESULFURIZATION SYSTEM
OPERATING CONDITIONS

VARIABLE	MONTHLY DATA AVERAGES					
	1/74	2/74	3/74	4/74	5/74	6/74
SO ₂ (PPM)						
IN	634.77	830.12	763.36	667.50	634.10	563.31
OUT	114.81				107.61	125.19
XRFMDV	81.27				82.58	76.98
PH	7.24	7.20	7.13	7.01	6.94	6.98
POWER PLANT RATE (MW)	113.35	136.05	139.33	130.30	136.36	127.59
DIFF. PRESSURES (IN. H ₂ O)						
TOTAL	8.23	7.02	6.47	5.90	5.53	6.25
WET	1.44	0.50	0.61	0.85	0.77	1.14
DRYER	0.05	0.05	0.06	0.07	0.07	0.08
TEMPERATURES (F)						
-ABSORBER						
INLET	293.55	299.63	287.88	294.26	287.04	287.23
GAS OUT	124.70	129.40	129.25	127.34	129.59	130.39
SLURR.	129.30	128.26	128.87	130.88	130.32	130.16
MGSLUR	176.27	173.79	177.77	179.24	176.74	177.10
-DRYER						
GAS OUT	420.83	426.30	426.02	408.77	400.37	394.82
PRDN.	341.62	349.96	334.36	320.47	321.86	318.27
FLOWS (GPM)						
CIRC.	14973.15	14274.07	15492.71	15421.59	15245.29	14725.40
CENTED	120.55	123.68	130.12	129.42	130.01	130.90
MGSLUR	23.55	17.67	14.65	13.96	20.19	16.98
CENTRIFUGE TORQ. (G>S)	22.81	16.90	13.36	12.27	10.87	7.15

TABLE 28
FLUE GAS DESULFURIZATION SYSTEM
STREAM ANALYSIS

VARIABLE	MONTHLY DATA AVERAGES					
	5+6/73	7/73	8+9/73	10/73	11/73	12/73
DRYER						
% SOL.	81.79	79.36	85.13	85.19	85.42	88.80
ΣMGS03	60.25	59.66	57.62	60.71	60.66	58.88
ΣMGS04	11.56	11.59	14.15	11.33	11.97	17.68
ΣMG0	3.58	4.07	7.07	5.41	4.94	7.66
CENTRIFUGE						
% SOL.	75.68	73.32	76.53	79.02	77.84	80.09
ΣMGS03	53.07	51.91	48.30	49.71	50.11	49.29
ΣMGS04	7.47	8.50	8.87	8.42	9.87	9.43
ΣMG0	2.01	2.59	4.15	2.95	2.83	3.27
RECYCLE						
% SOL.	10.49	12.92	10.49	12.84	11.01	13.64
PH	6.95	7.40	7.27	7.36	7.19	7.20
-FILTRATE						
ΣMGS03	1.05		1.03		1.00	
ΣMGS04	16.56	13.88	0.00	15.81	16.46	16.66
-CAKE						
ΣMGS03	52.67	52.02				
ΣMGS04	4.94	5.63		4.26		
ΣMG0	2.79	3.53	4.10	4.41	3.05	3.15
MOTHER LIQUOR						
% SOL.	3.44	5.67	4.21	5.47	5.53	8.29
-CAKE						
ΣMGS03	38.69	32.33				
ΣMGS04	9.71	13.71				
ΣMG0	4.30	5.26	4.34	5.20	3.30	3.73

TABLE 28 (CONT'D)
FLUE GAS DESULFURIZATION SYSTEM
STREAM ANALYSIS

VARIABLE	MONTHLY DATA AVERAGES					
	1/74	2/74	3/74	4/74	5/74	6/74
DRYER						
% SOL.	88.57	87.61	85.41	87.51	89.93	86.78
% H ₂ SO ₃	65.00	65.89	64.05	60.70	63.98	59.93
% H ₂ SO ₄	16.36	11.61	17.32	11.10	11.68	14.77
% H ₂ O	2.78	3.47	3.39	5.75	4.09	3.44
CENTRIFUGE						
% SOL.	86.01	81.27	82.20	79.50	79.17	78.57
% H ₂ SO ₃	46.61	48.64	46.93	46.20	47.56	45.84
% H ₂ SO ₄	10.13	6.75	6.86	7.33	8.07	10.47
% H ₂ O	1.21	1.47	1.70	3.61	2.43	2.06
RECYCLE						
% SOL.	11.90	7.54	8.39	10.37	8.24	7.86
PH	7.11	7.18	7.19	7.21	7.13	7.17
-FILTRATE						
% H ₂ SO ₃						
% H ₂ SO ₄	15.83	12.41	13.73	15.98	16.69	18.58
-CAKE						
% H ₂ SO ₃						
% H ₂ SO ₄						
% H ₂ O	1.73	1.82	3.03	3.96	2.97	2.26
MOTHER LIQUOR						
% SOL.	8.37	3.53	4.62	6.57	3.13	3.12
-CAKE						
% H ₂ SO ₃						
% H ₂ SO ₄						
% H ₂ O	2.10	2.25	3.75	4.00	4.93	4.03

TABLE 29
REGENERATION SYSTEM
OPERATING CONDITIONS

VARIABLE	MONTHLY DATA AVERAGES					
	5+6/73	7/73	8+9/73	10/73	11/73	12/73
CALCINER						
-TEMPERATURES (F)						
WOKTIN	1221.72	1228.00	1189.51	1091.74	1001.24	983.28
GASOUT	650.27	665.56	588.73	569.41	555.66	563.23
PROOFV	159.01	178.80	117.12	161.33	202.57	149.07
-SOLID FLOWS (PPH)						
MGS03	63.87	59.99	66.35	72.05	76.81	65.47
COKE	0.84	0.97	0.25	0.0	0.0	0.0
NEUT. PH LTO.	5.64	5.25	5.51	5.24	5.75	5.53
ACID PLANT FEED GAS (%)						
CO	0.10	0.17	n.a.	n.a.	n.a.	n.a.
O2	6.96	5.20	10.25	4.43	4.29	3.69
SO2	3.58	n.a.	n.a.	n.a.	n.a.	n.a.

TABLE 29(CONT'D)
REGENERATION SYSTEM
OPERATING CONDITIONS

VARIABLE	MONTHLY DATA AVERAGES					
	1/74	2/74	3/74	4/74	5/74	6/74
CALCINER						
-TEMPERATURES(F)						
WALL	958.45	1045.89	1005.60	1019.45	1072.56	1052.75
GAS OUT	538.55	571.66	546.98	550.53	560.16	538.03
PROXY	154.72	192.23	168.95	165.42	179.00	172.61
-SOLID FLOWS (PPM)						
MGSO3	62.60	76.81	76.45	77.80	77.00	78.94
COKE	0.0	0.0	0.0	0.0	0.0	0.0
NEUT. PH LIO.	5.72	5.11	5.19	5.68	5.72	5.66
ACID PLANT						
FEED GAS(%)						
CO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
O2	5.01	5.36	5.31	4.49	4.97	4.66
SO2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

TABLE 30
REGENERATION SYSTEM
STREAM ANALYSIS

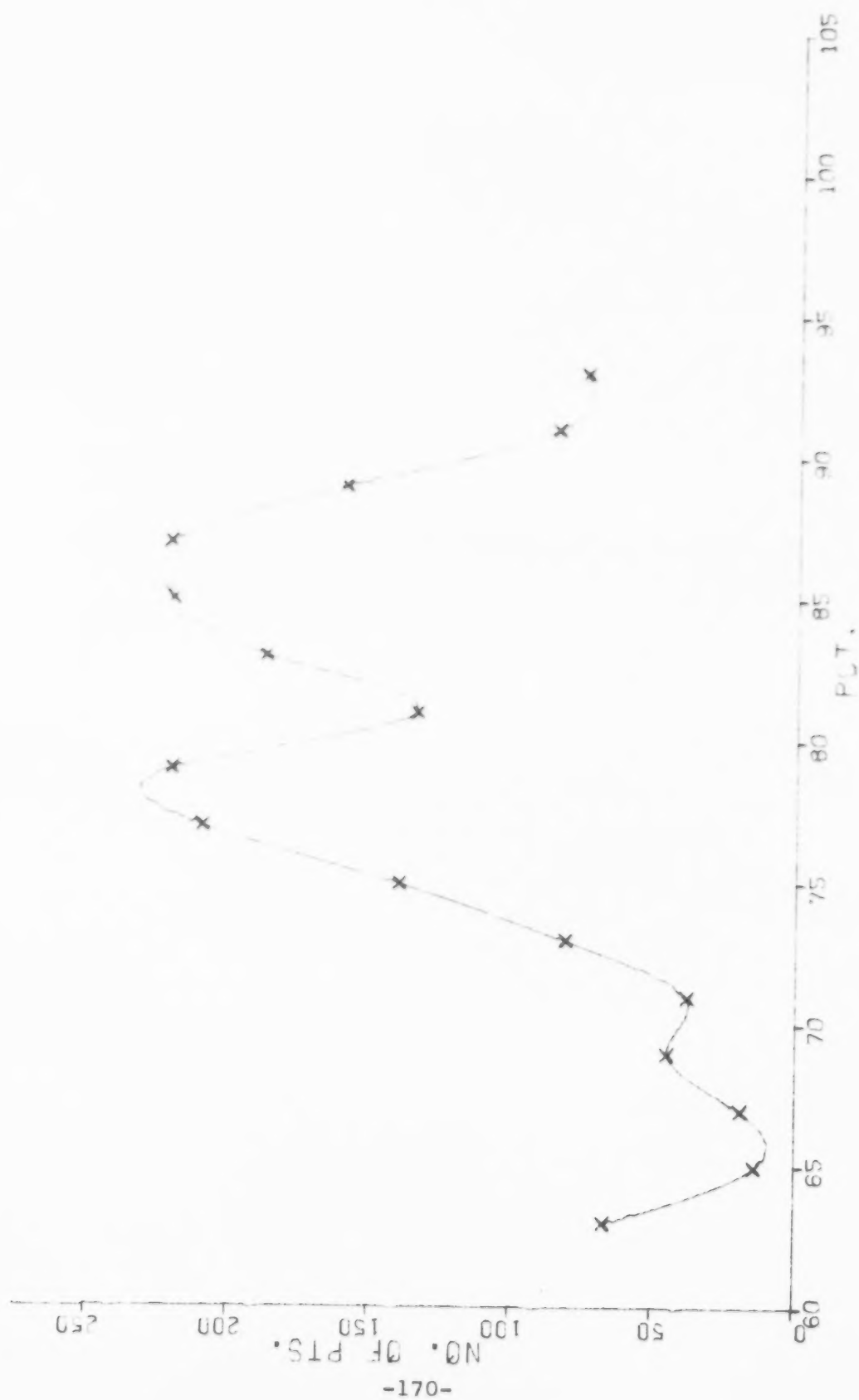
VARIABLE	MONTHLY DATA AVERAGES					
	5-6/73	7/73	8+9/73	10/73	11/73	12/73
CALCINED FEED						
XMG01	16.47	17.79	16.86	14.88	15.56	13.20
XMG503	58.90	58.92	57.30	59.83	59.09	61.53
XMG500	10.31	10.93	11.52	12.63	12.54	12.38
XMG02	7.56	7.52	8.52	6.69	7.28	7.78
XCA288	n.a.	n.a.	n.a.	1.05	0.81	0.45
CALCINED PRODUCT						
XMG503	0.06	0.02	0.0	0.04	0.0	0.01
XMG500	5.38	6.05	8.71	10.47	10.91	8.28
XMG01	21.24	49.59	93.38	85.66	84.04	86.11
SO2EFF	52.27	47.33	23.43			
RLK05M	28.30	31.33	40.18	34.08	34.04	49.46

TABLE 30(CONT'D)
REGENERATION SYSTEM
STREAM ANALYSIS

VARIABLE	MONTHLY DATA AVERAGES					
	1/74	2/74	3/74	4/74	5/74	6/74
CALCINED FEED						
X H2O	12.68	9.86	13.33	15.76	12.70	15.20
XMGSO3	65.31	64.64	64.13	58.38	61.97	58.66
XMGSO4	10.95	10.13	6.92	9.22	11.95	11.87
XMG I	5.36	6.84	6.79	7.80	4.78	5.75
XCAH3N	1.65	1.02	2.05	1.06	1.04	1.13
CALCINED PRODUCT						
XMGSO3	0.00	0.02	0.37	0.0	0.0	0.12
XMGSO4	17.52	16.75	4.37	4.22	12.42	7.60
XMG O	84.13	86.93	88.21	90.10	83.80	86.69
SO2 EFF		34.00				
RIK DEN	17.65	27.76	24.02	32.58	20.85	25.80

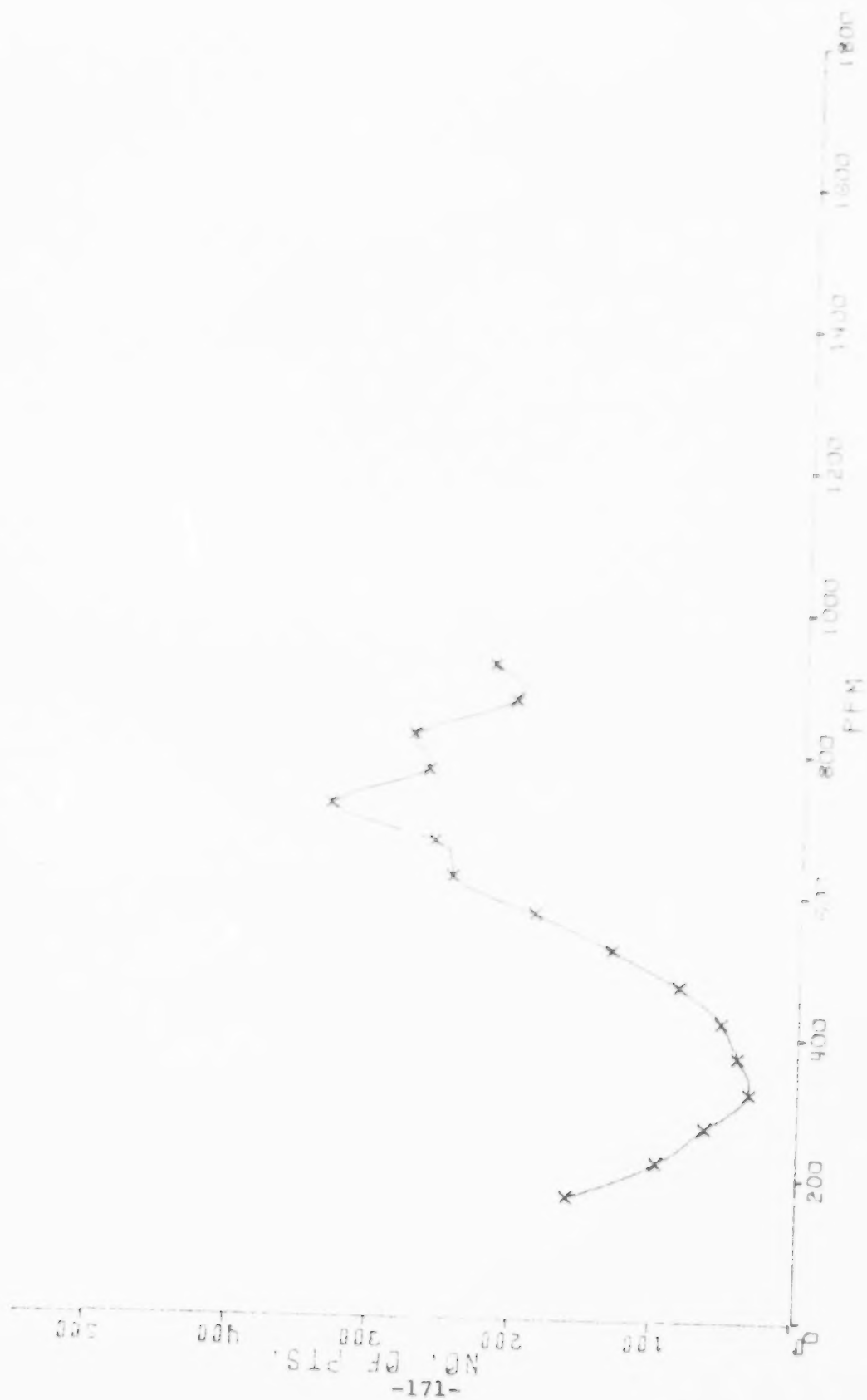
9.2

RANGE OF SIGNIFICANT VARIABLES

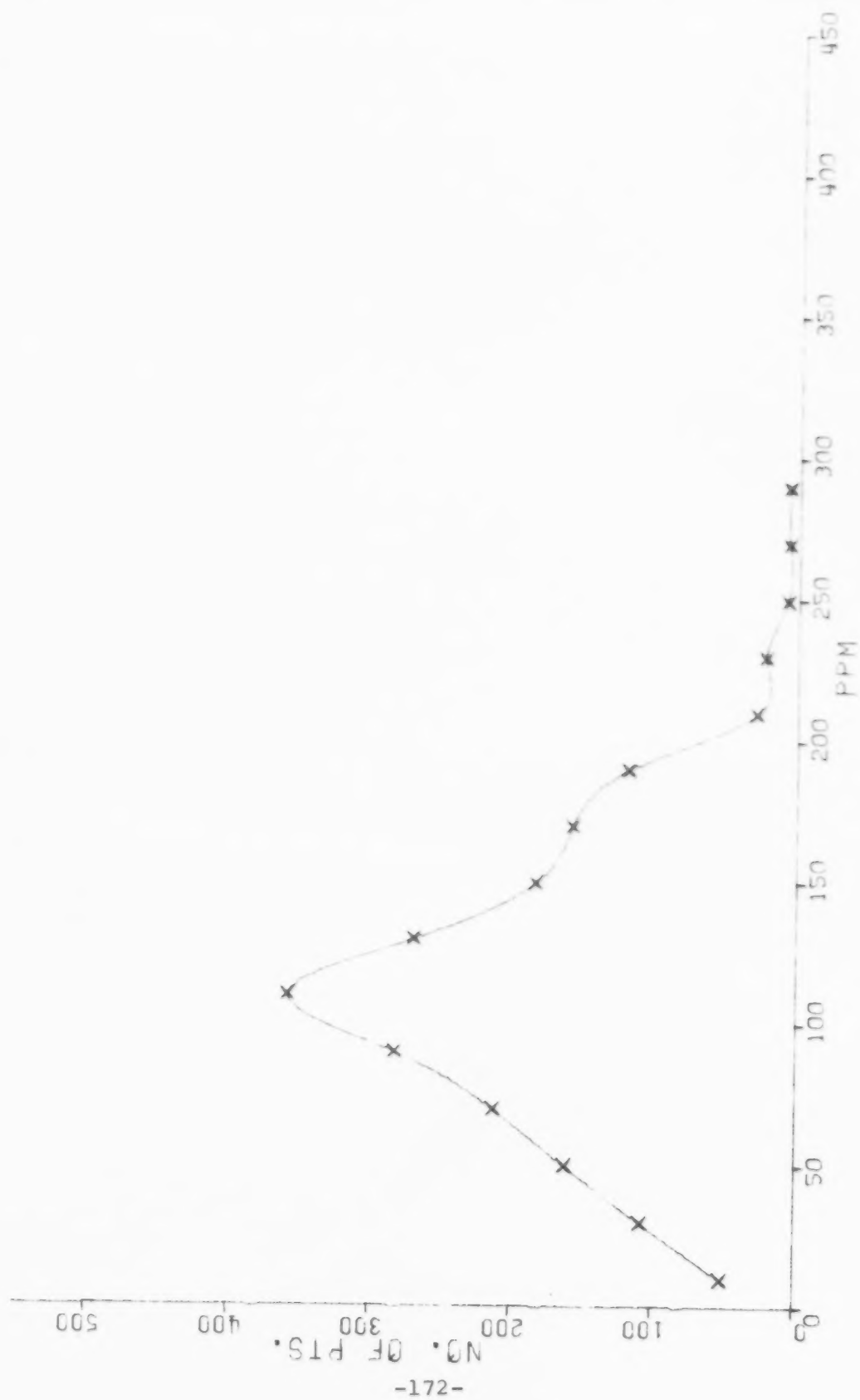


BOSTON ED. OPERATION - SO₂ REMOVAL EFF.
FREQUENCY DISTRIBUTION

Fig. 37



BOSTON ED. OPERATION - 500 IN ET LONG.
 FREQUENCY DISTRIBUTION

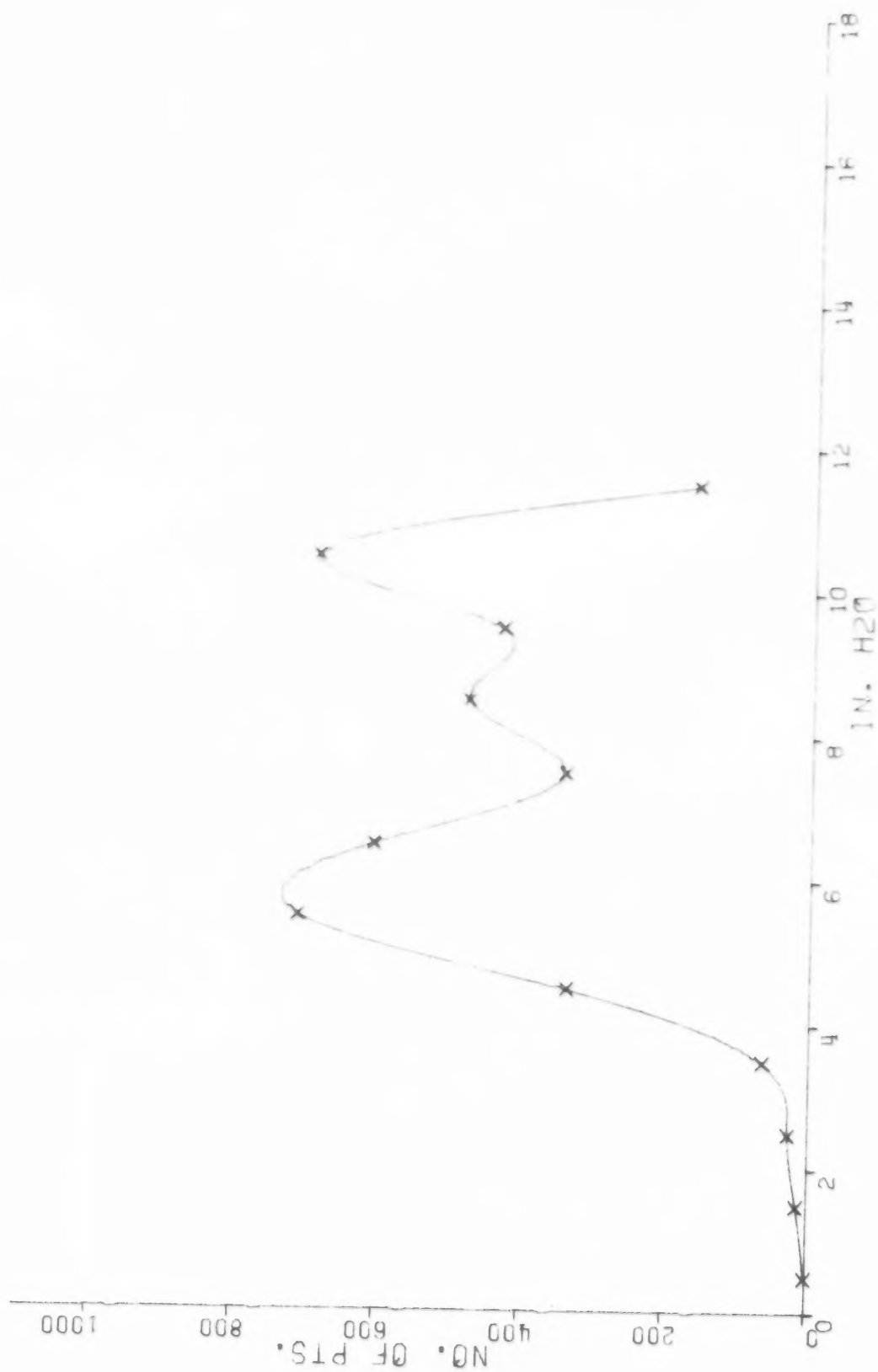


BOSTON ED. OPERATION - SO2 OUTLET CONC.
FREQUENCY DISTRIBUTION



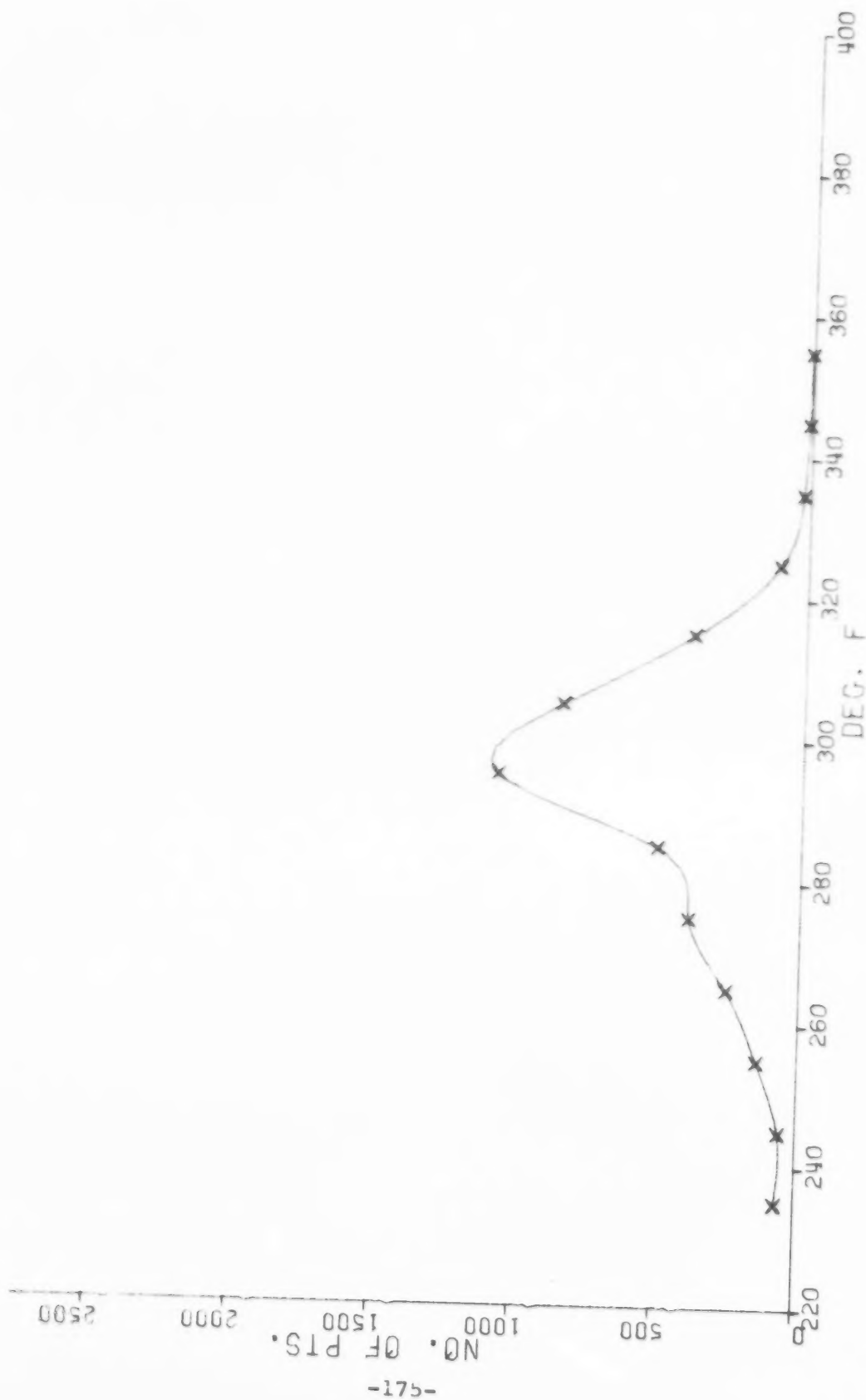
BOSTON ED. OPERATION - NW L.
FREQUENCY DISTRIBUTION

Fig. 40



BOSTON ED. OPERATION - TOTAL DELTA P
FREQUENCY DISTRIBUTION

Fig. 41

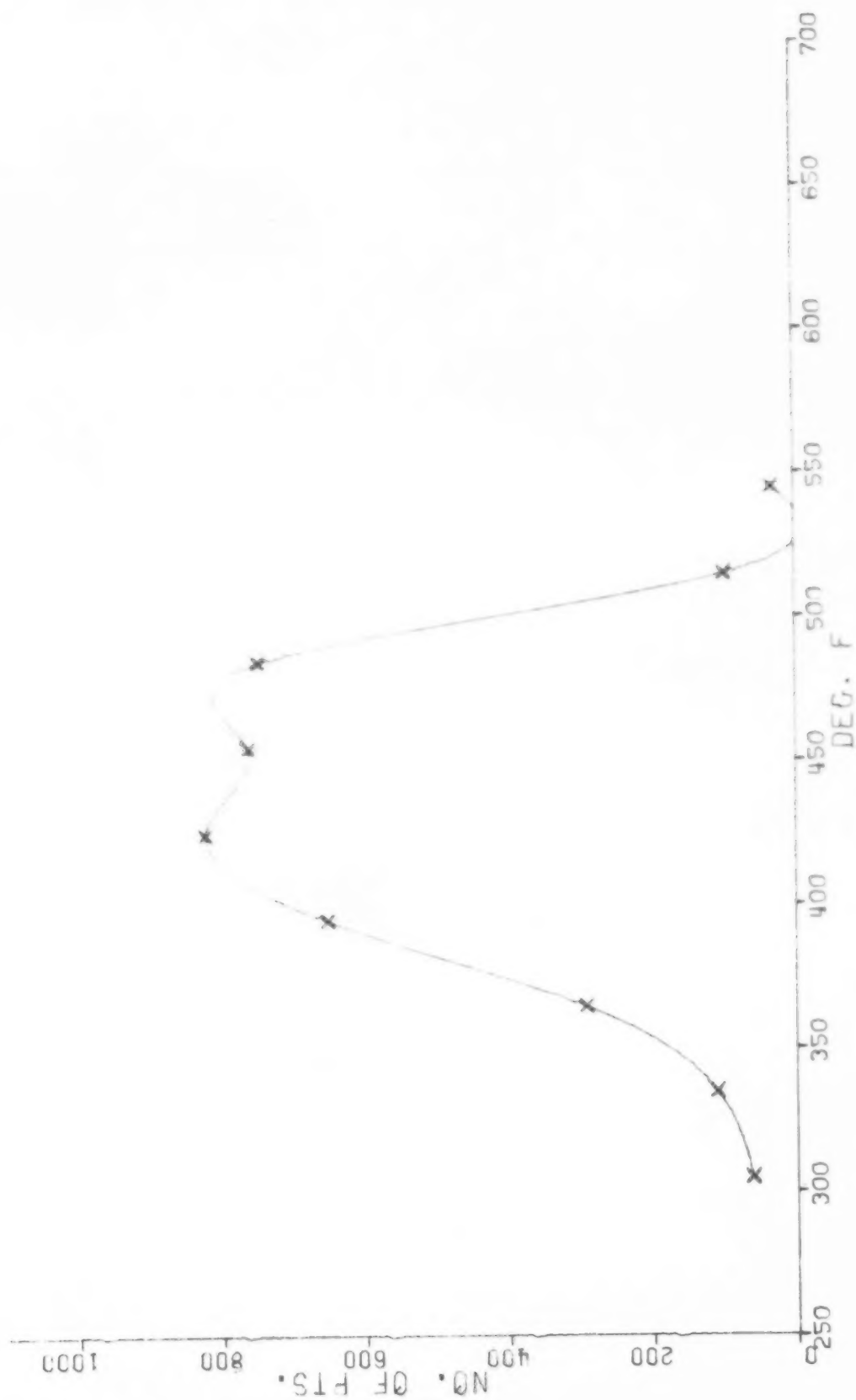


BOSTON ED. OPERATION - ABSORB. INLET TEMP.
FREQUENCY DISTRIBUTION



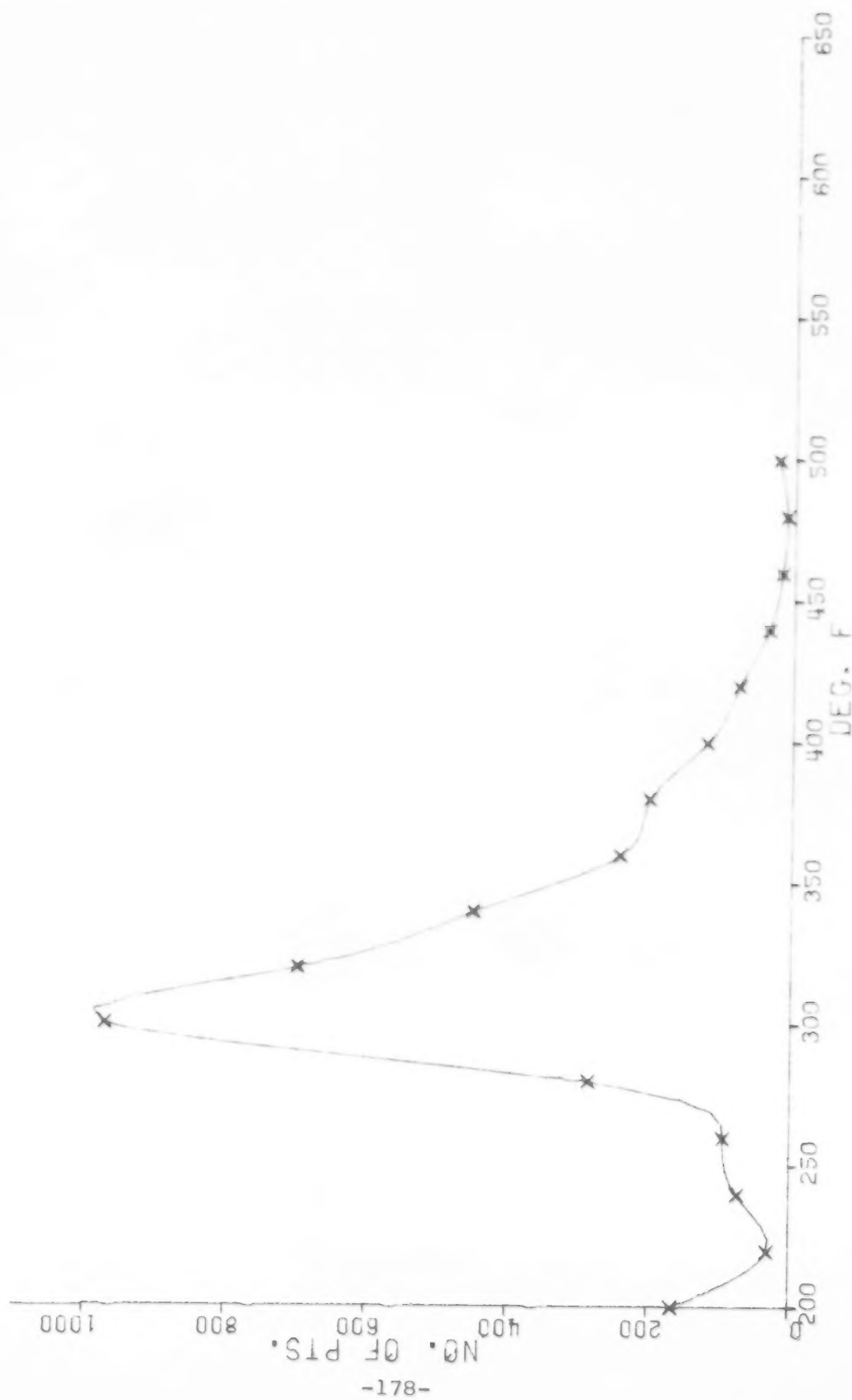
BOSTON EL. OPERATION
FREQUENCY DISTRIBUTION

Fig. 43



BOSTON ED. OPERATION - DRYER GAS OUT TEMP
FREQUENCY DISTRIBUTION

Fig. 44

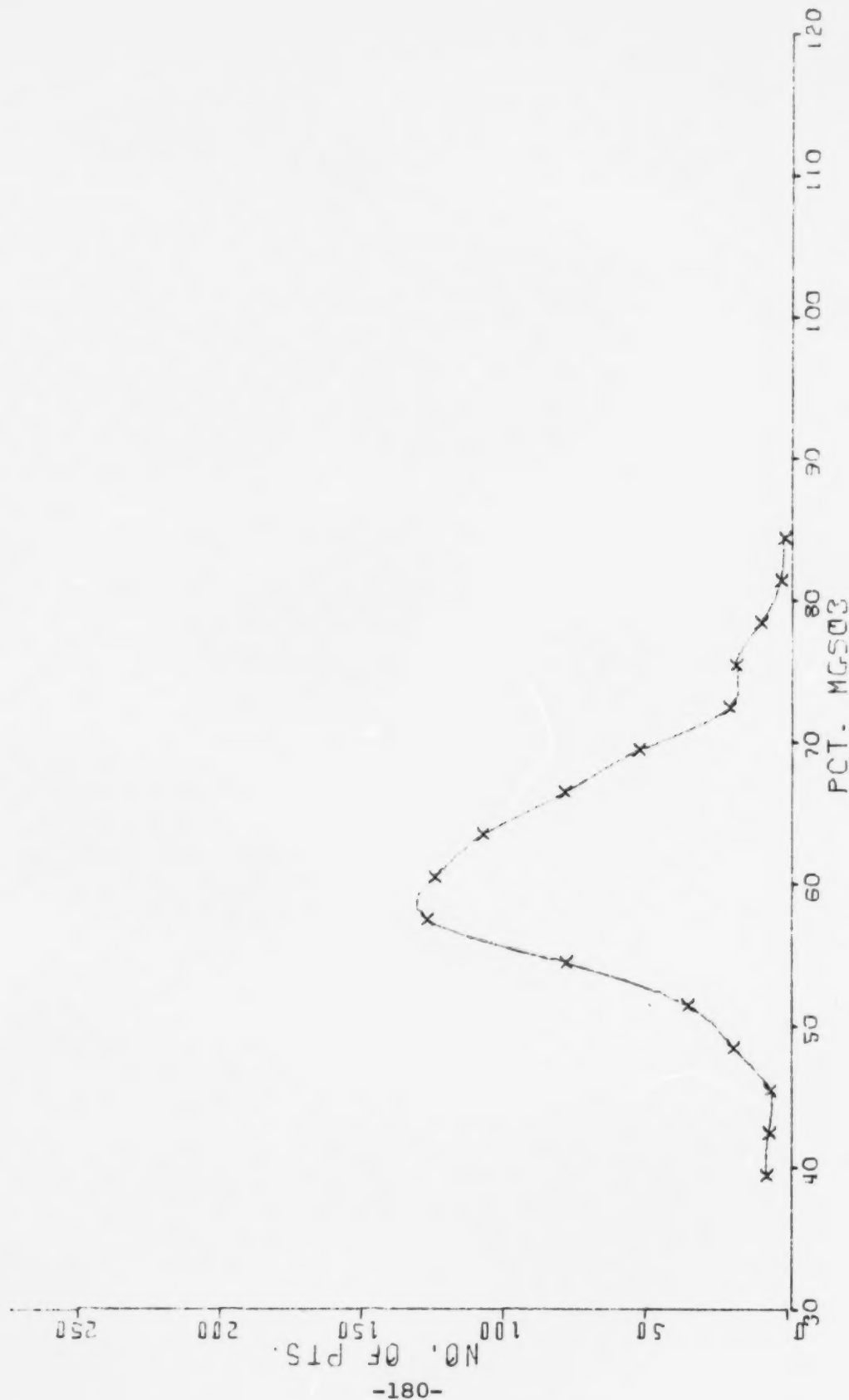


BOSTON ED. OPERATION - DRYER PRODUCT TEMP
FREQUENCY DISTRIBUTION

Fig. 45

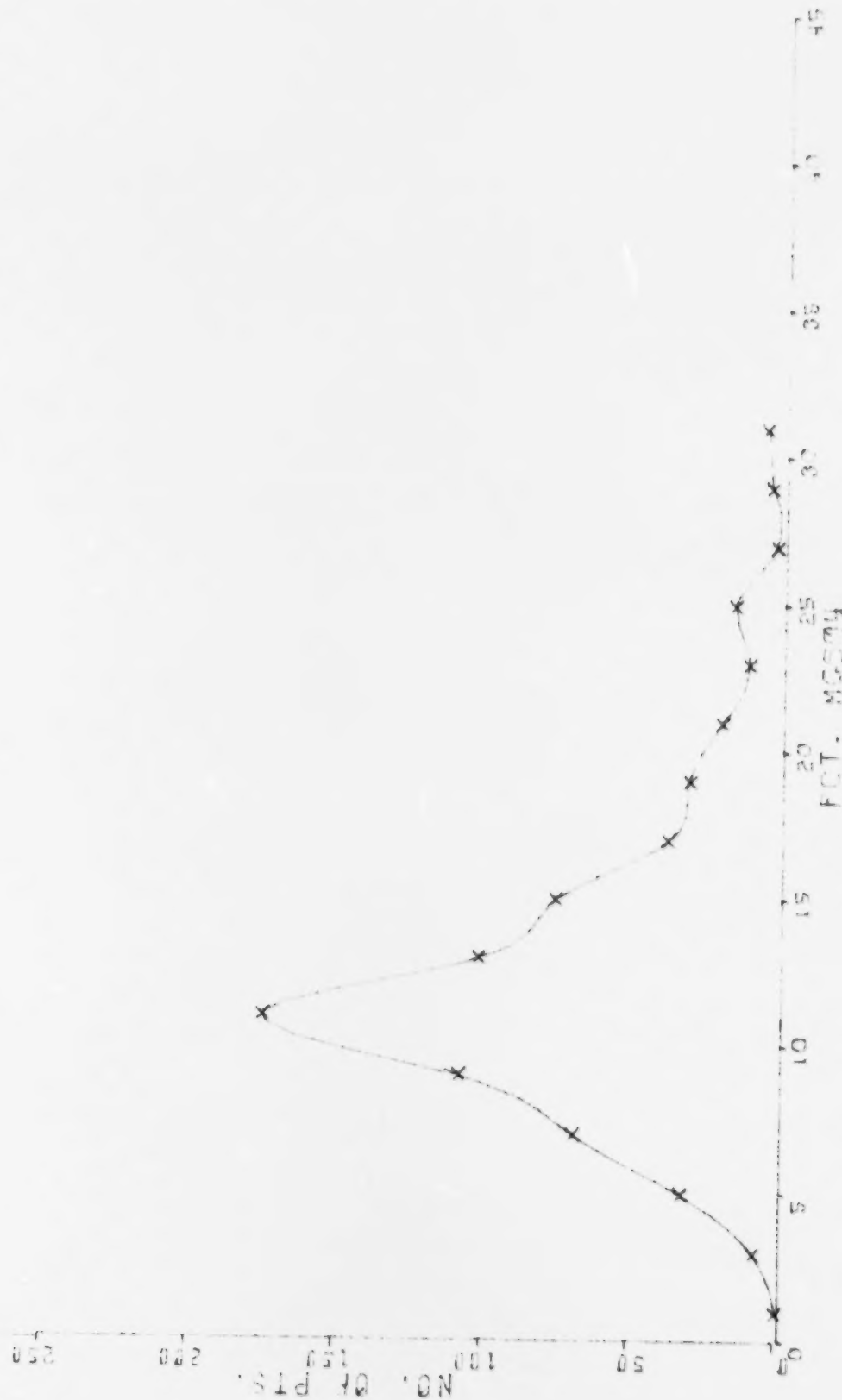


BOSTON ED. OPERATION - PRAYER PRODUCT
FREQUENCY DISTRIBUTION



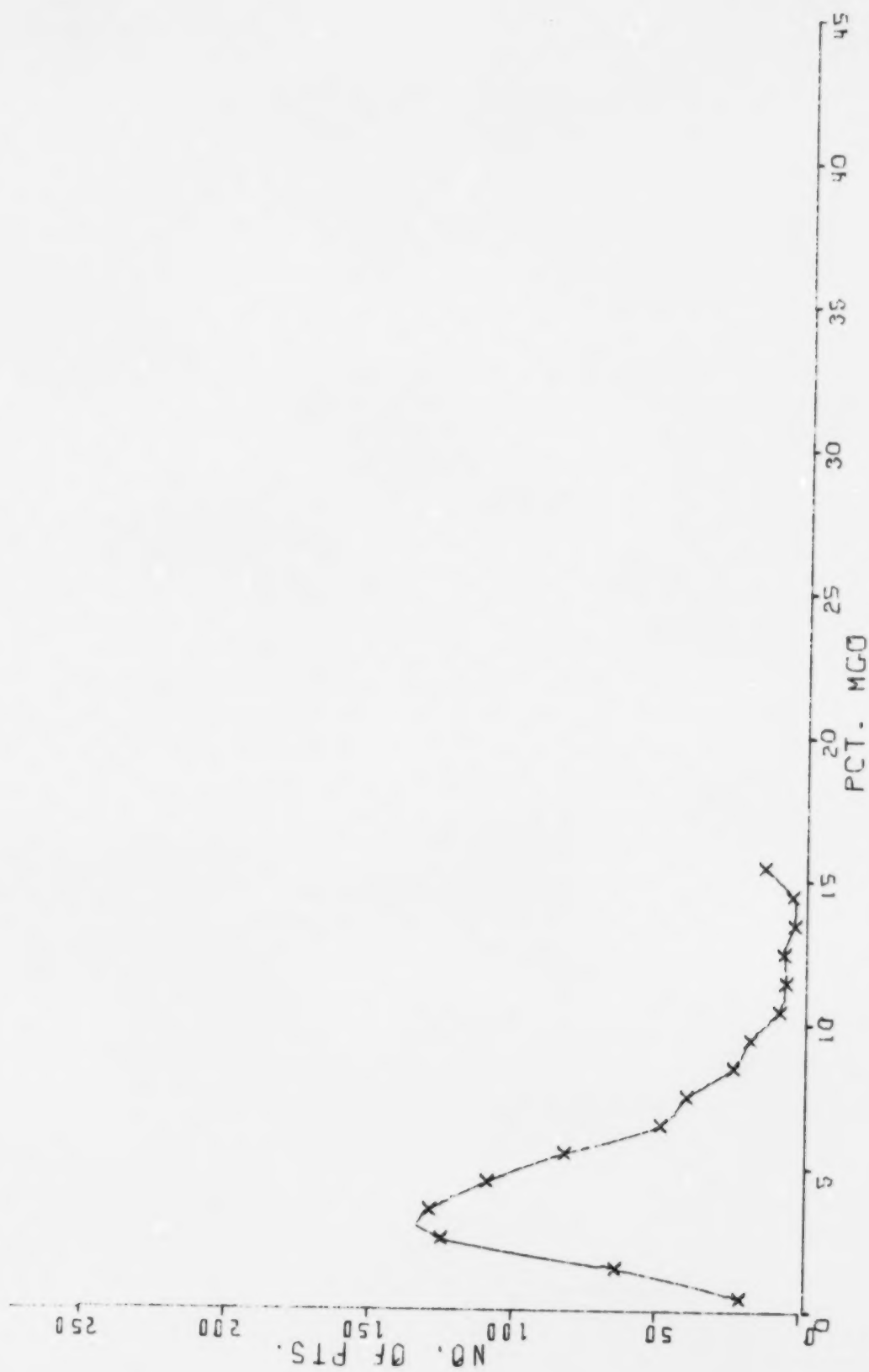
BOSTON ED. OPERATION - DRYER PRODUCT
FREQUENCY DISTRIBUTION

Fig. 47



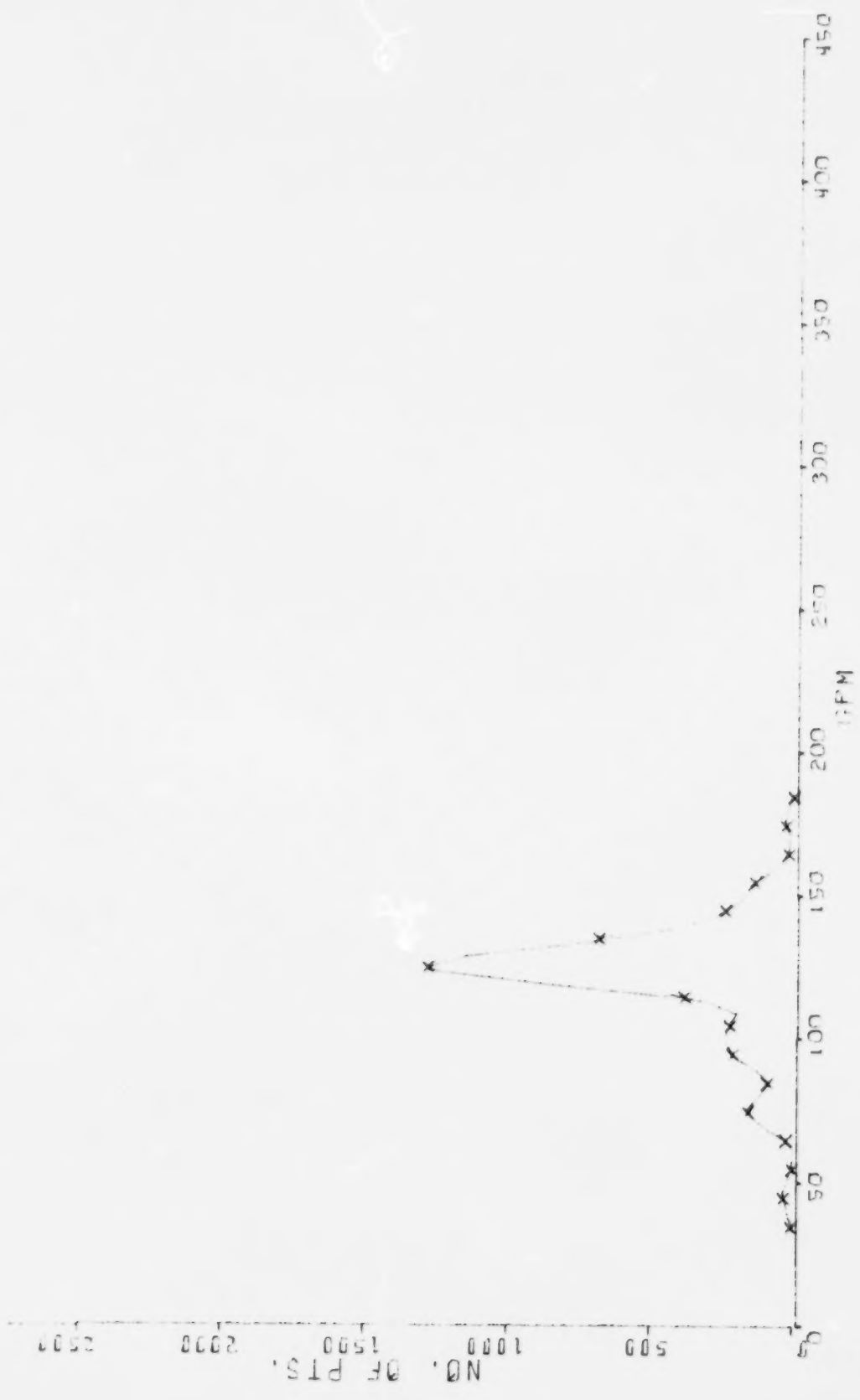
BOSTON ED. OPERATION - 1st YEAR PRODUCT
FREQUENCY DISTRIBUTION

Fig. 48



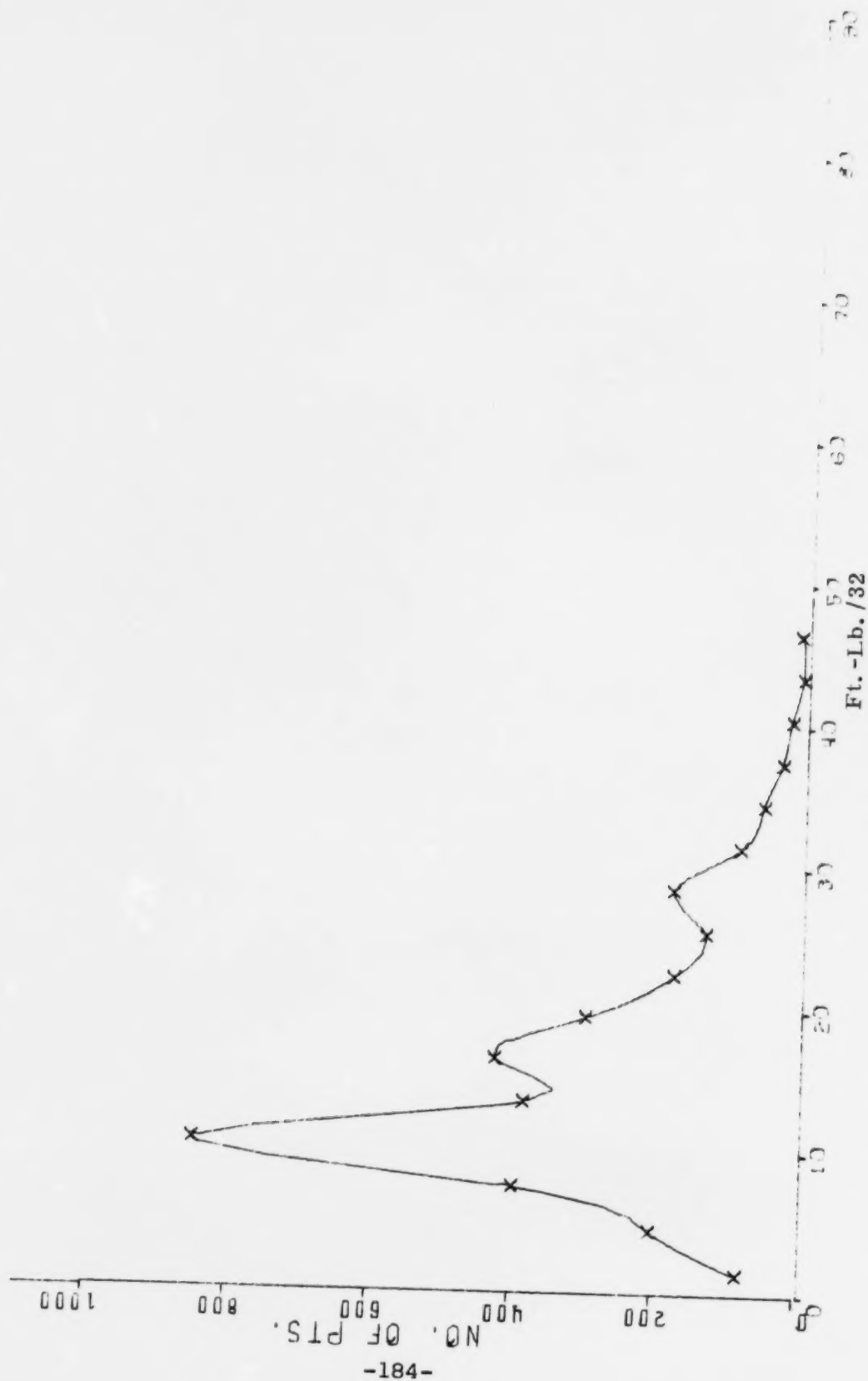
BOSTON ED. OPERATION - DRYER PRODUCT
FREQUENCY DISTRIBUTION

Fig. 49



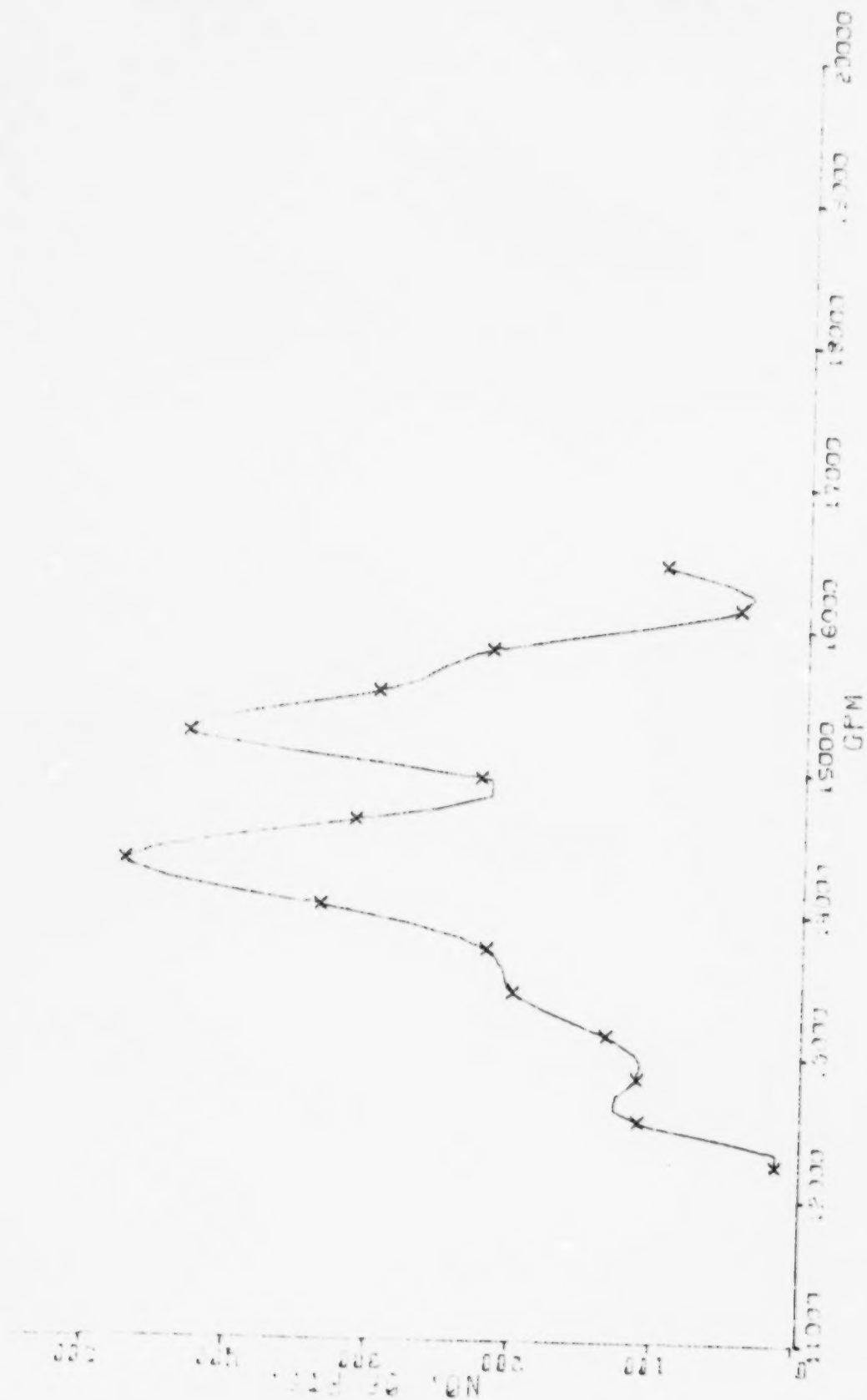
BOSTON ED. OPERATION - CENTRIFUGE FEED
FREQUENCY DISTRIBUTION

Fig. 50



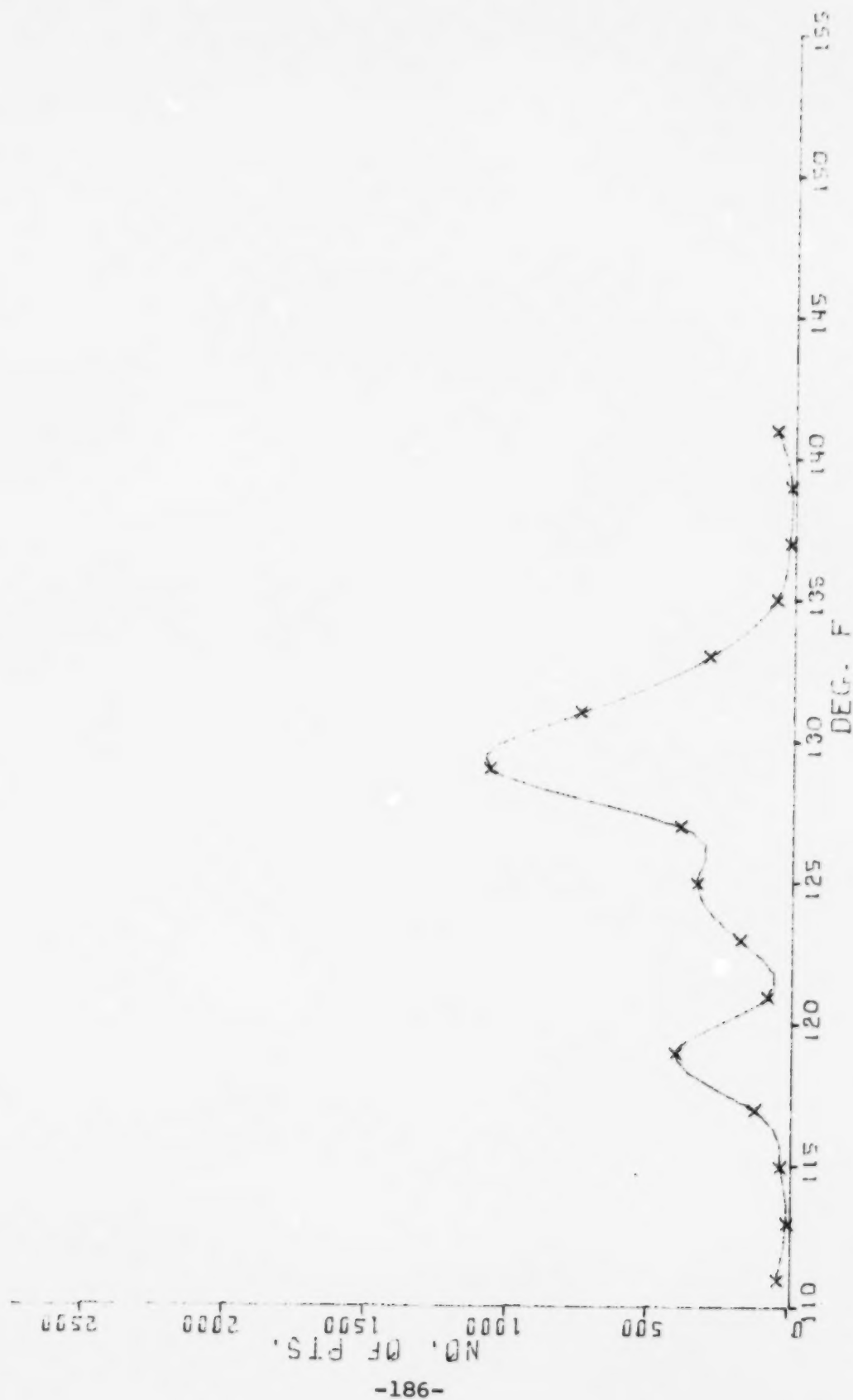
BOSTON ED. OPERATION - CENTRIFUGE TORQUE
FREQUENCY DISTRIBUTION

Fig. 51



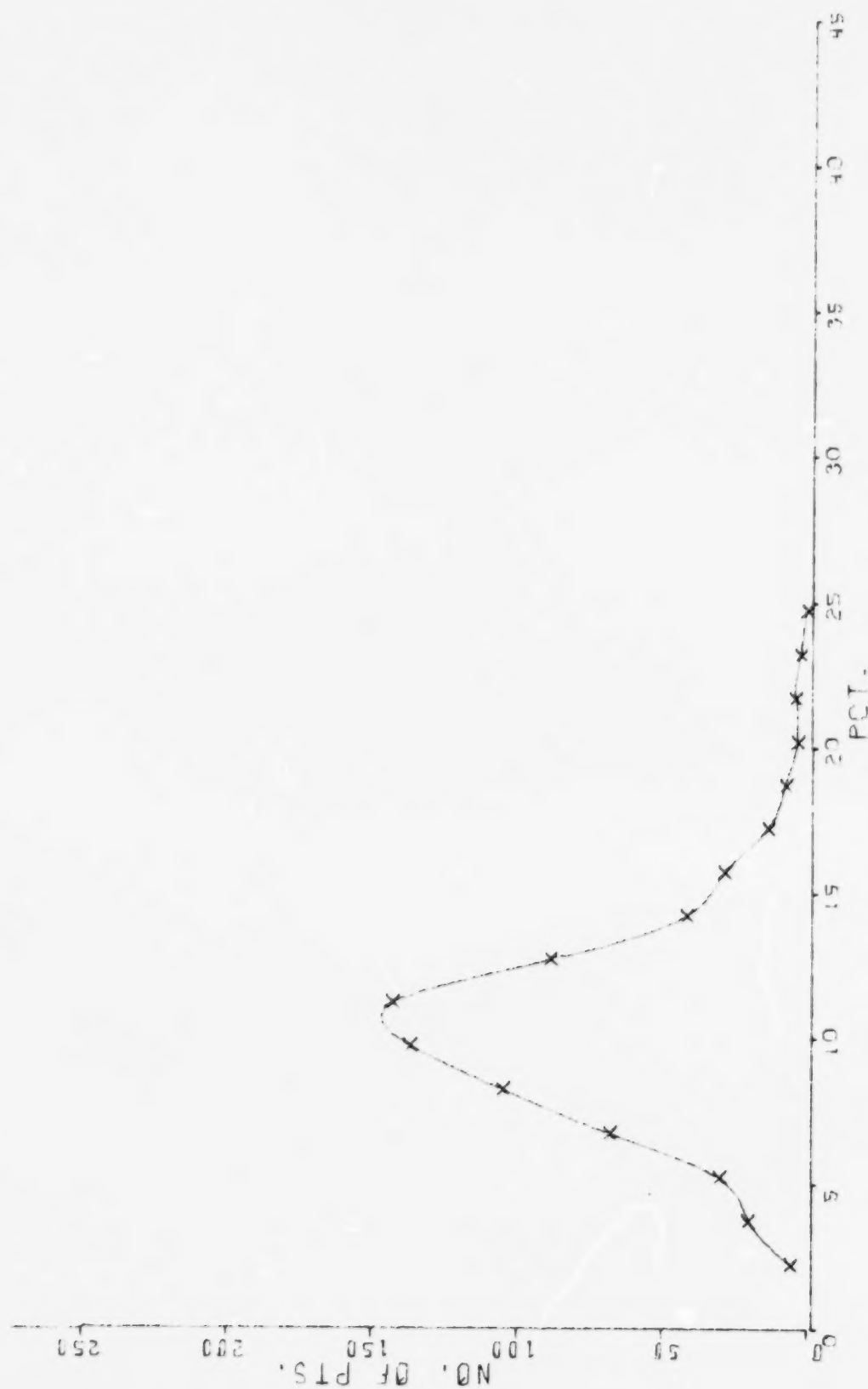
BOSTON ED. OPERATION - RECY. LINE
FREQUENCY DISTRIBUTION

Fig. 52



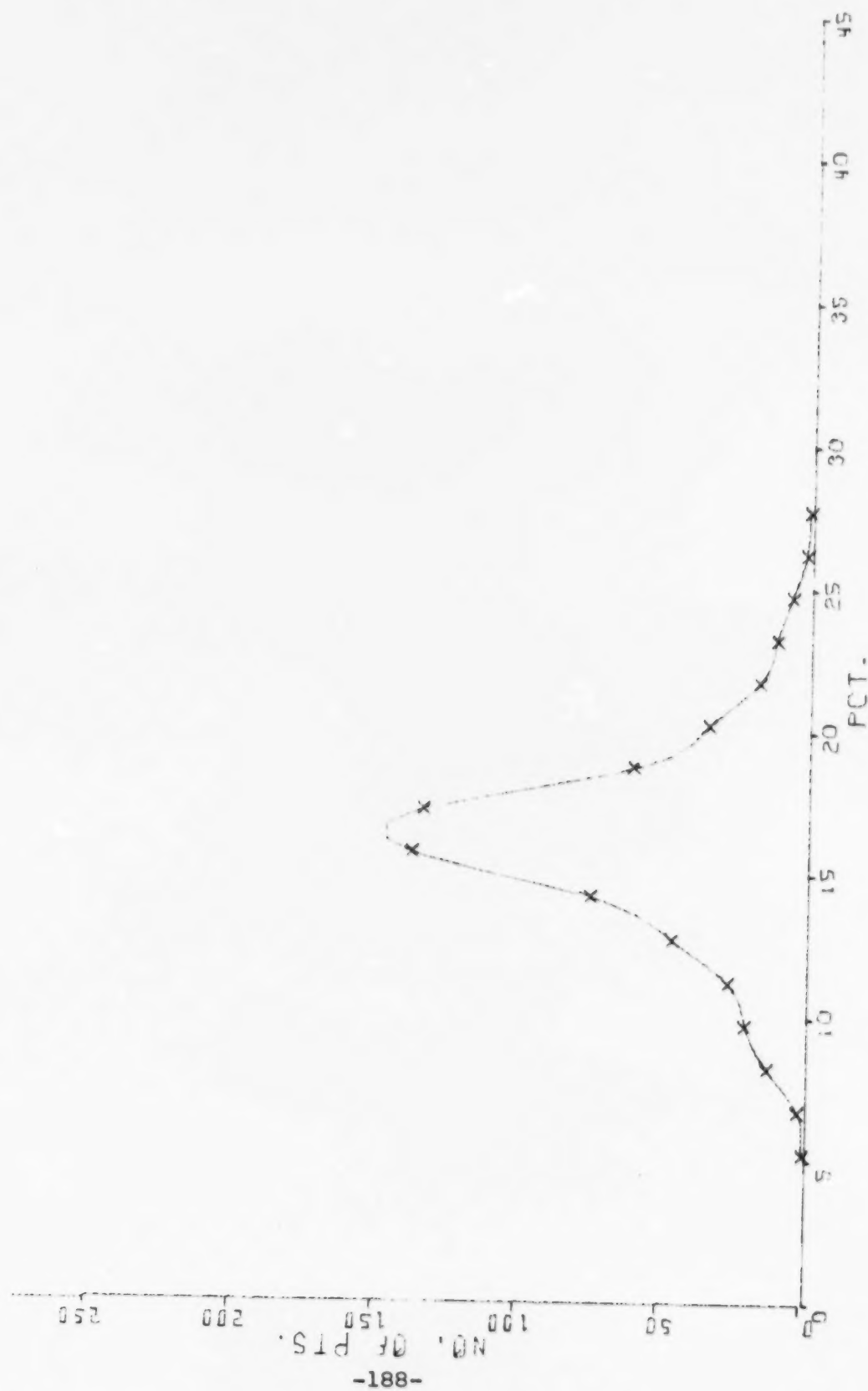
BOSTON ED. OPERATION - RECY. SLUR. TEMP.
FREQUENCY DISTRIBUTION

Fig. 53

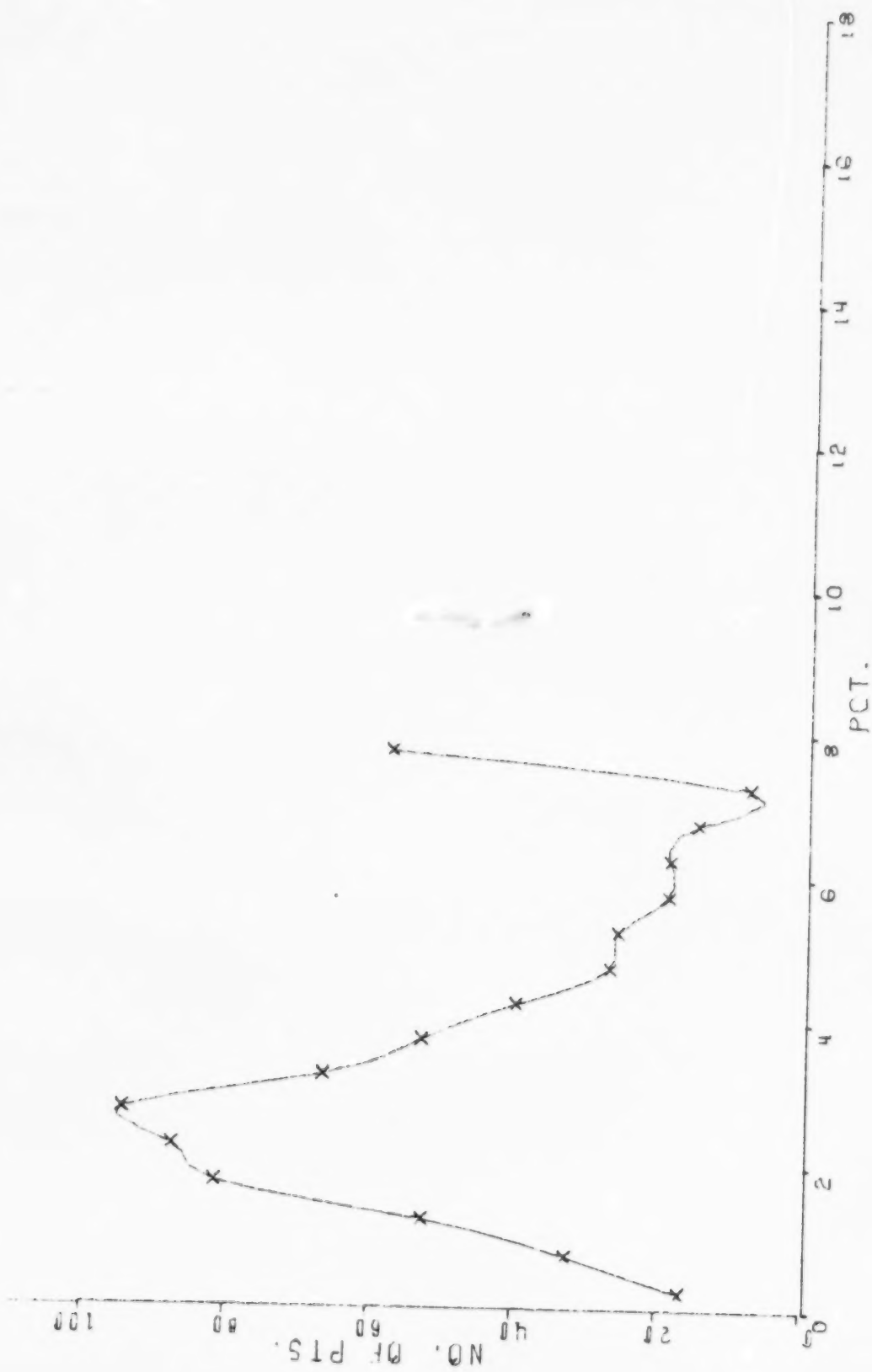


BOSTON ED. OPERATION - RECYCLE SOLIDS
FREQUENCY DISTRIBUTION

Fig. 54

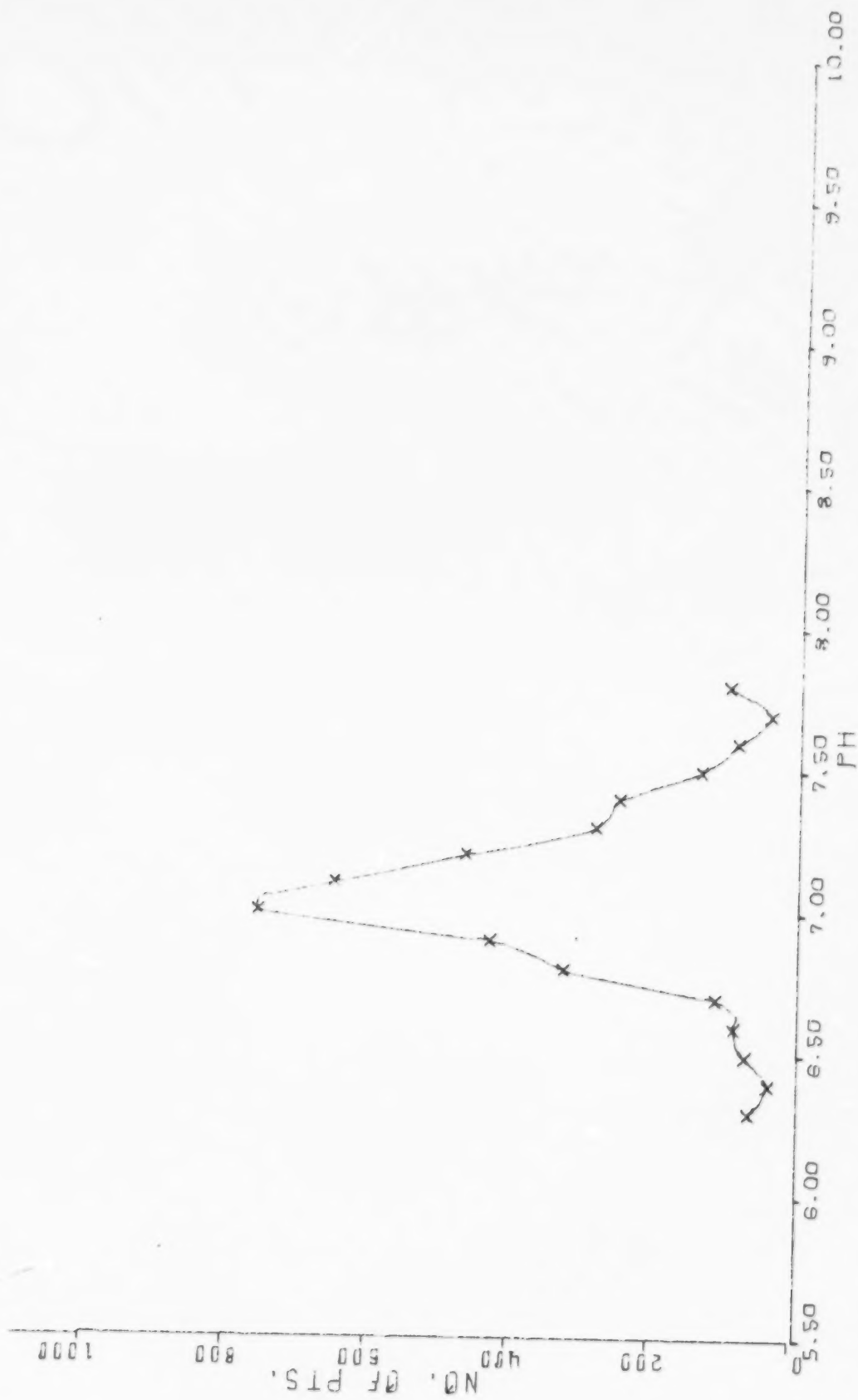


BOSTON ED. OPERATION - RECYCLE MGS04
FREQUENCY DISTRIBUTION



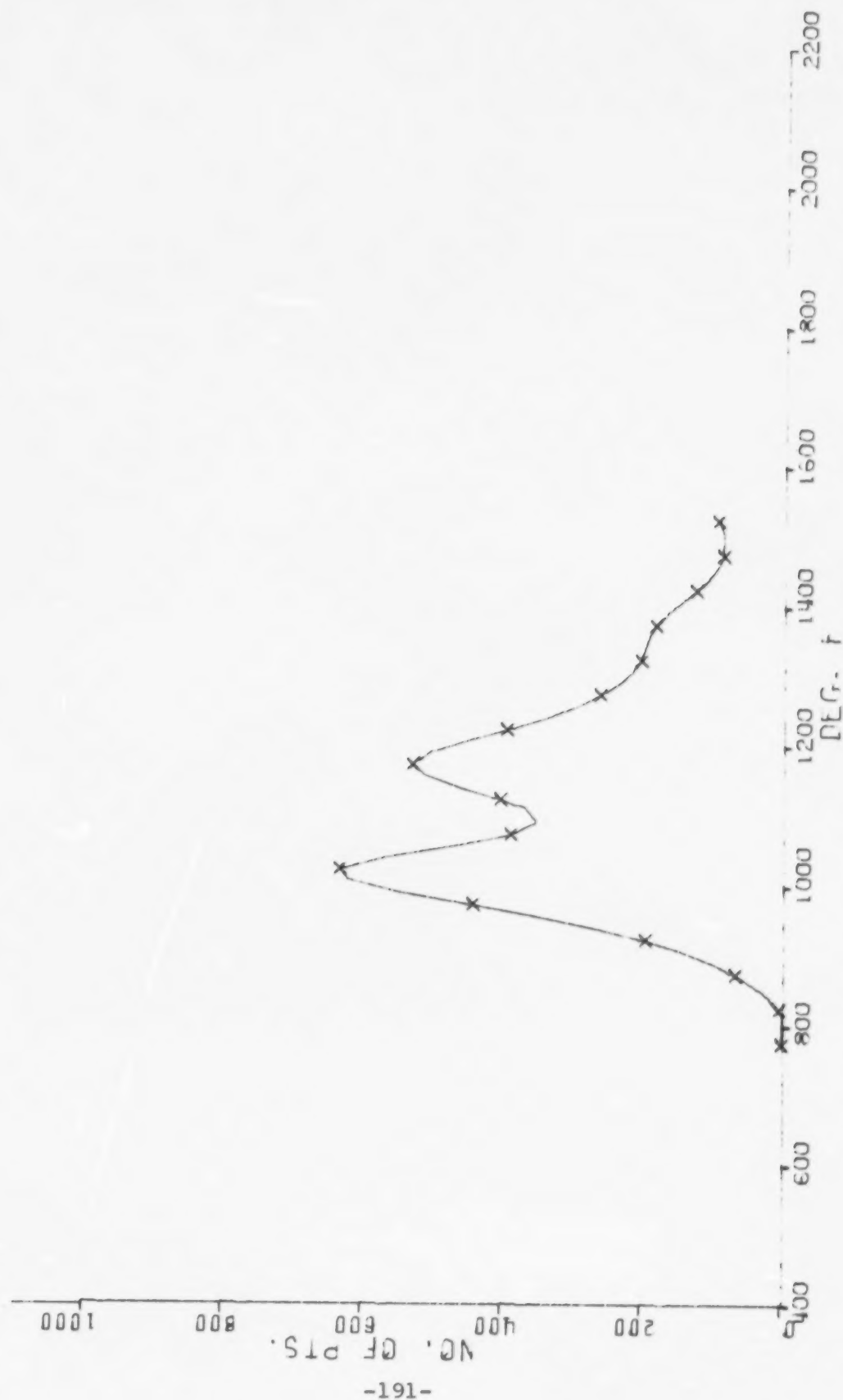
BOSTON ED. OPERATION - RECYCLE 1000
FREQUENCY DISTRIBUTION

Fig. 56



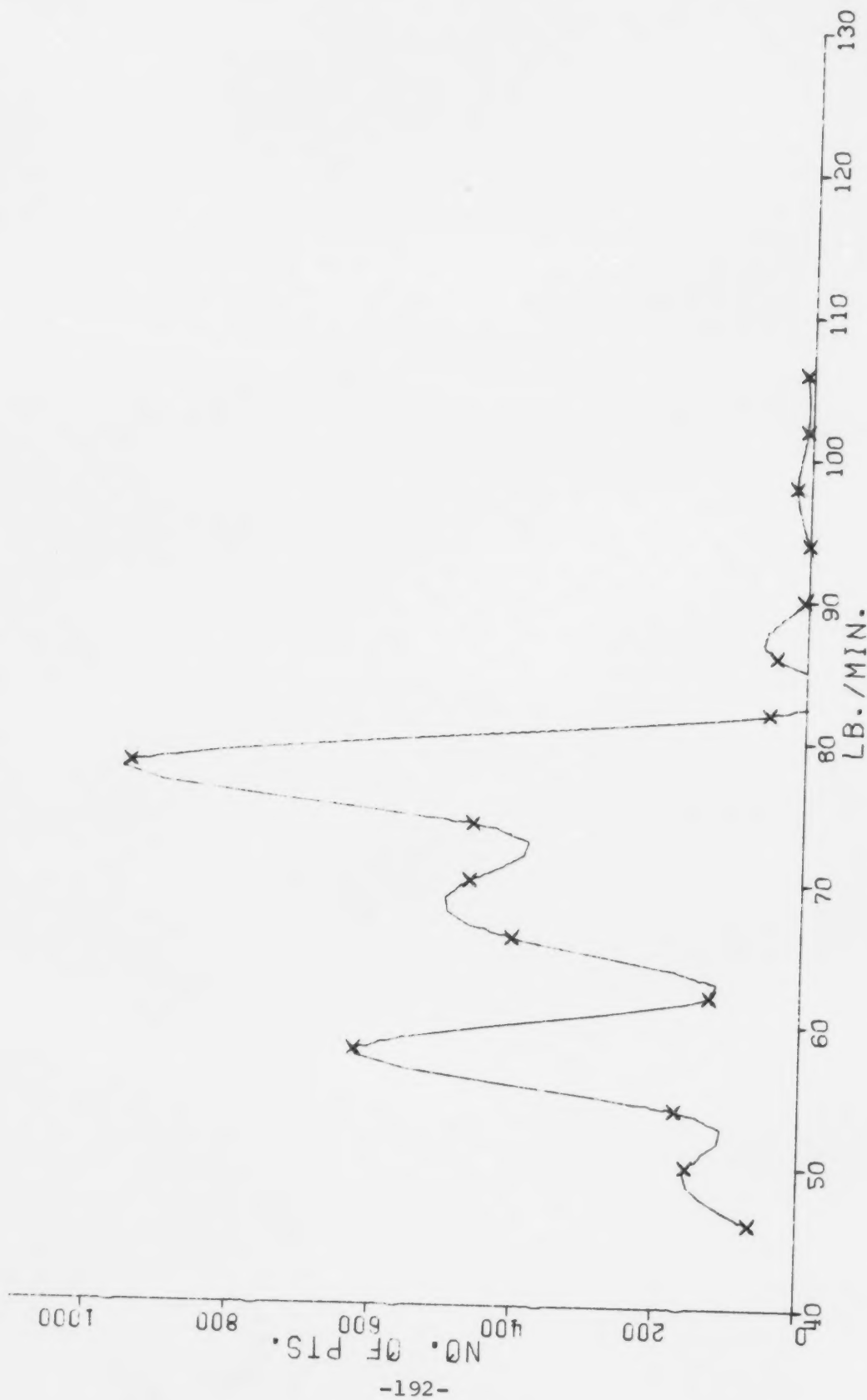
BOSTON ED. OPERATION - RECY. PH
FREQUENCY DISTRIBUTION

Fig. 57



CALCINER OPERATION - MIDKILN TEMP.
FREQUENCY DISTRIBUTION

Fig. 58



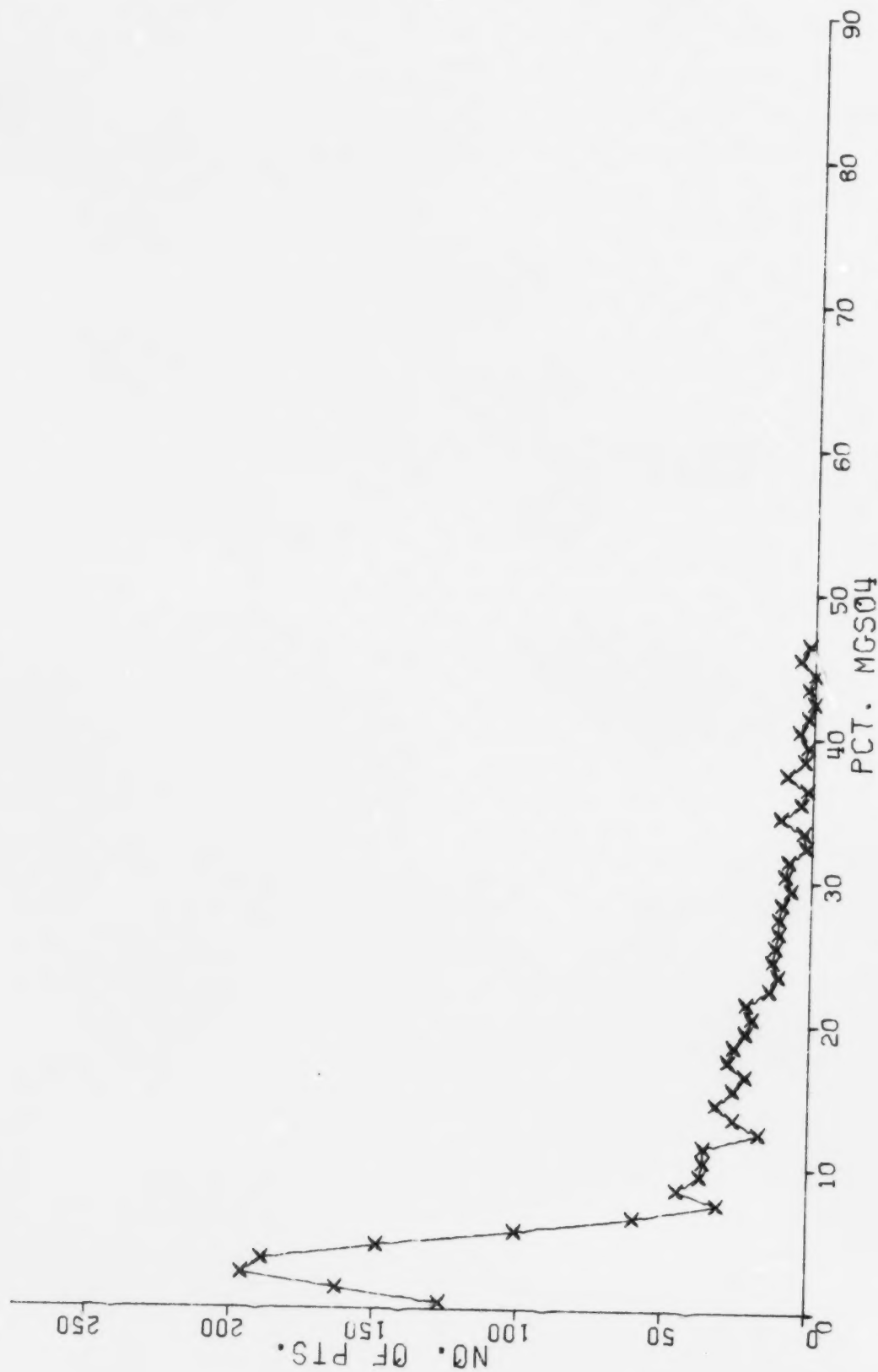
CALCINER OPERATION - MGS03 FEED RATE
FREQUENCY DISTRIBUTION

Fig. 59



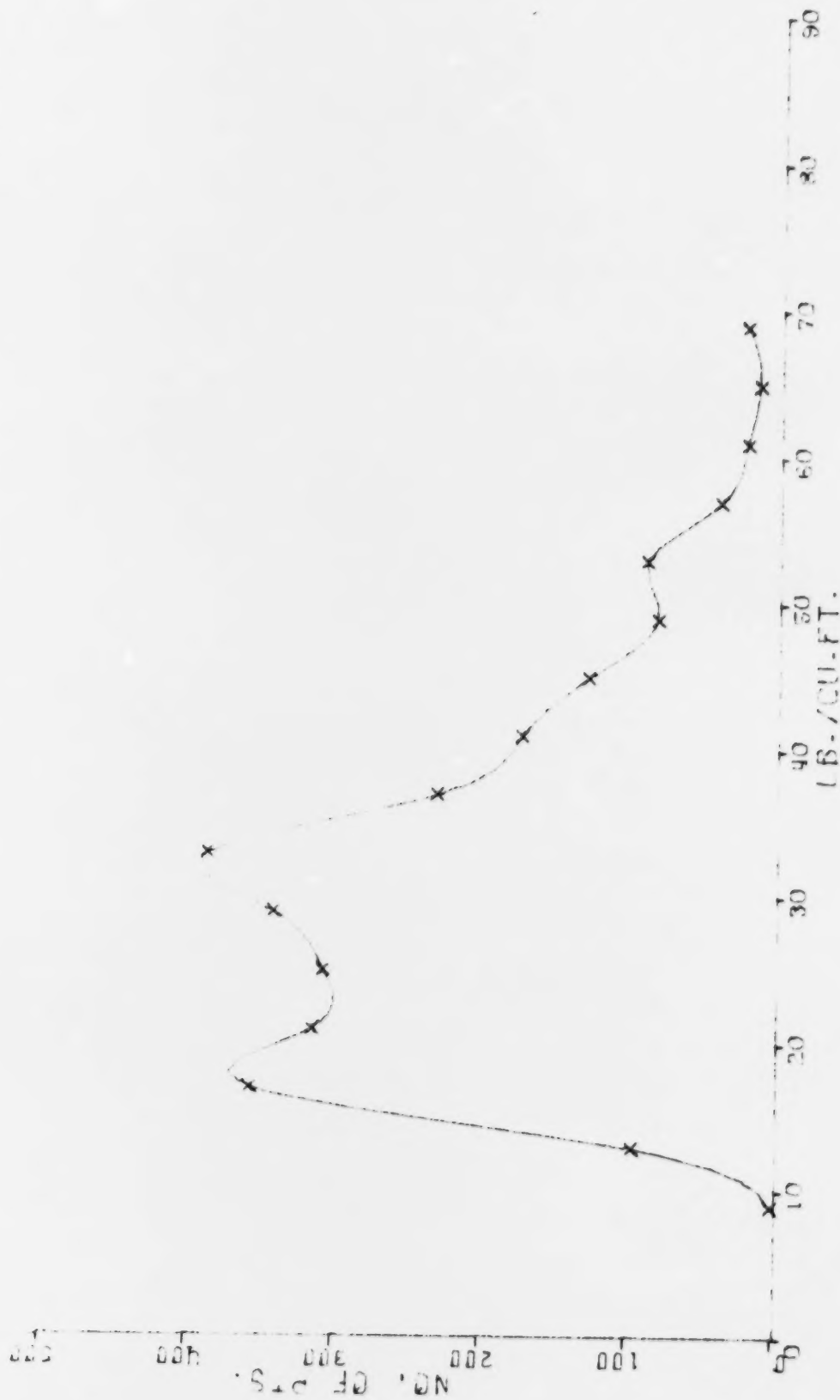
CALCINER OPERATION -- PRODUCT ANALYSIS
FREQUENCY DISTRIBUTION

Fig. 60



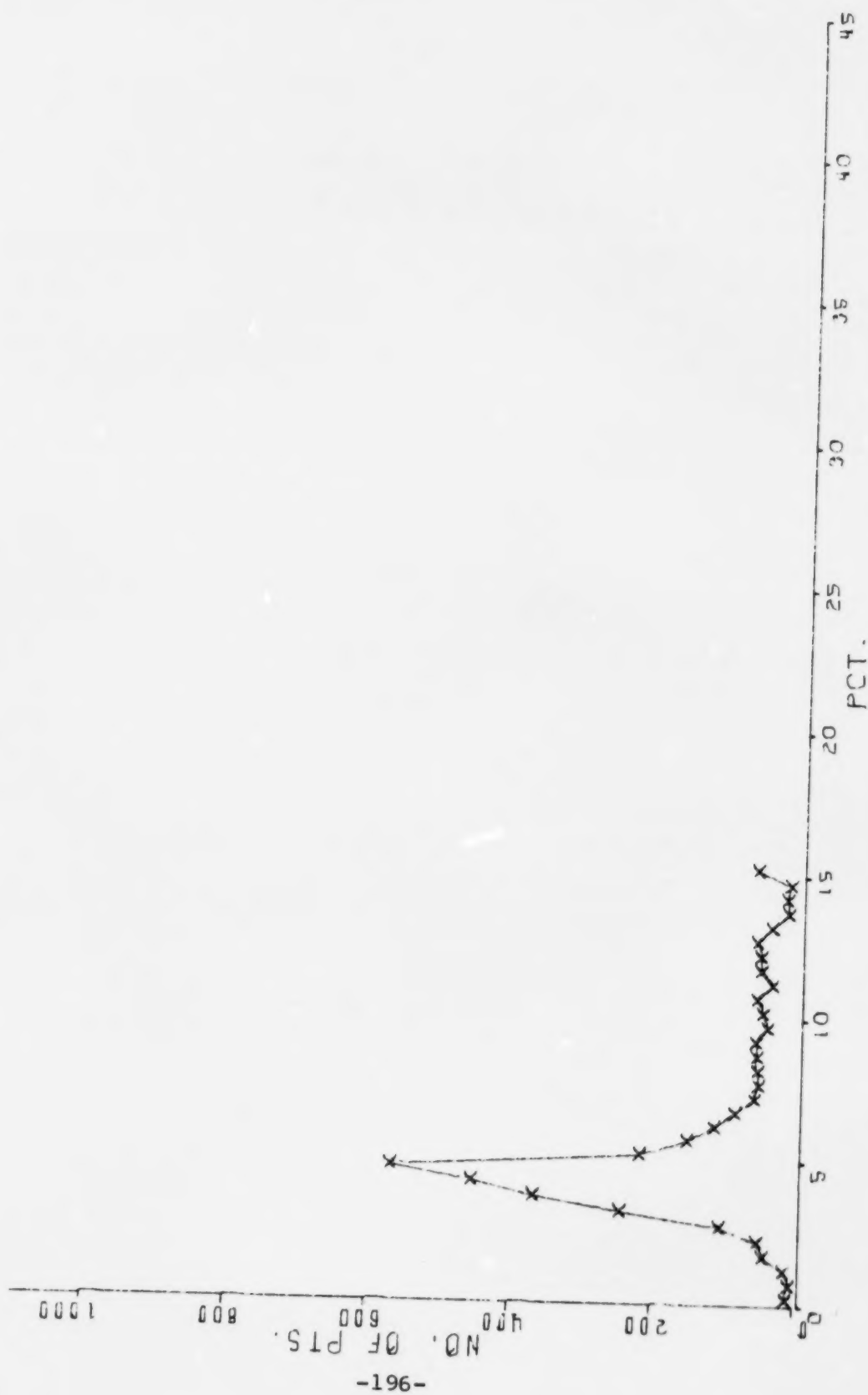
CALCINER OPERATION - PRODUCT ANALYSIS
FREQUENCY DISTRIBUTION

Fig. 61



CALCINER OPERATION - PRODUCT BULK DENS.
FREQUENCY DISTRIBUTION

Fig. 62



CALCINER OPERATION - ACID
FREQUENCY DISTRIBUTION

Fig. 63

9.3

MISCELLANEOUS DATA

TABLE 31

MYSTIC STATION
UNIT #6
% SULFUR - #6 FUEL OIL

	% S		% S
April 72	1.72	Jan. 73	2.04
May 72	1.86		2.08
	1.86		2.11
	1.93		2.05
	1.88	Feb. 73	2.08
June 72	1.93		2.07
	1.91		2.17
	1.91		2.17
	2.05	March 73	2.11
July 72	2.05		2.13
	2.03		2.11
	2.08		2.12
	2.05	April 73	2.08
Aug. 72	2.00		2.10
	2.14		2.05
	2.09	May 73	2.10
	2.09		2.06
	1.99		2.09
Sept. 72	2.03	June 73	2.10
	2.10		2.06
	2.04		2.05
	2.01		1.73
Oct. 72	2.01	July 73	2.04
	2.01		2.08
	1.81		1.95
	1.97		2.13
Nov. 72	2.00	Aug. 73	2.00
	2.04		2.08
	1.96		2.10
	2.04		2.11
	2.02		2.08
Dec. 72	1.96	Sept. 73	2.03
	2.01		2.05
	2.10		2.07
	2.09		2.02

TABLE 31 (CONT'D)
STATION #200 - UNIT #6

	% S
Oct. 73	2.10 2.07 1.95 2.15
Nov. 73	2.25 2.13 2.19 2.11 2.13
Dec. 73	2.16 2.25 2.19 2.18
Jan. 74	2.23 2.13 2.15 2.03 2.03
Feb. 74	1.92 2.02 2.02 2.11 2.02
March 74	2.05 1.97 1.88 1.90
April 74	1.96 1.86 1.60 1.81
May 74	1.98 1.85 1.65 1.67
June 74	1.60 1.58 1.88 1.91

TABLE 32

HIGH SULFUR OIL ASH ANALYSIS

METHOD OF TEST: Emission Spectroscopy

SAMPLE IDENTIFICATION: Sample #1235

Ash, % 0.046

Semi-Quantitative Spectrographic Analysis of Ash:

Vanadium	A
Nickel	3B
Sodium	B
Tin	3C
Silicon	3C
Calcium	C
Iron	C
Magnesium	C
Aluminum	3D
Boron	3D
Barium	3D
Cobalt	3D
Cadmium	3D
Copper	D
Chromium	D
Molybdenum	D
Lead	D
Strontium	D
Titanium	D
Manganese	3E
Silver	E

Key: A = Greater Than 10%

B = 1 - 10%

C = .1 - 1.0%

D = .01 - .1%

E = .001 - .01%

F = .0001 - .001%

G = Less Than .0001%

3B = Three Times Letter Value

TABLE 33

REGENERATED MgO VANADIUM AND NICKEL CONTENT

<u>Date</u>	<u>% Vanadium</u>	<u>% Nickel</u>
6-12-73	0.43	0.085
7-3-73	0.55	0.100
7-19-73	0.69	0.093
7-27-73	1.55	0.374
9-12-73	0.45	0.136
11-5-73	1.00	0.134
11-6-73	0.80	0.170
12-4-73	0.83	0.08
12-5-73	0.83	0.08

10.0 FINANCIAL DATA

Project costs are presented in this section for the plants construction and for their operation, this data is summarized in Table 34. A description of some guide lines and recommendations for the operating requirements of future plants is also presented and used in a comparison with cost data developed in a separate study to provide a basis for economic evaluation of the process.

TABLE 34
SUMMARY OF FINANCIAL DATA

	Systems Cost	Pre Start Up Through Break In Period	PERIOD		
			Planned Operational Testing	Continuous Operations	Project Termination Total
10.1					
	Chemico - Basic Magnesia F.C.D. System at Missile Station	\$3,635,000			
	Regeneration Plant and Acid Plant Modification	2,294,220			
	Tail Gas Scrubber	238,110			
	Total System Cost	\$6,167,330			
10.2					
	System Operation				
	F.C.D. System Operation & Maintenance	\$ 573,591	\$ 619,418	\$326,116	\$ 89,843
	Regeneration Plant Operation and Maintenance	747,717	578,716	391,364	1,717,997
	Project Management	488,872	260,800	94,300	34,582
	TOTAL OPERATIONS COST	\$1,810,180	\$1,458,934	\$812,260	\$124,425
					\$4,205,799

10.1 SYSTEMS COST

The costs of the prototype plants are presented for the F. G. D. System in Table 35 and for the regeneration system plus the cost of modifications to the acid plant in Table 36.

These are broken down to show total costs by specific categories identified by Chemico standard codes. (The equipment included in each of these sections has been listed in Tables 11 and 12 of Section 5).

10.1.1 System Cost Details

Table 35

MAGNESIA F. G. D. SYSTEM

Chemico Cost Code	Description	Cost *
A	Foundations	\$ 229,456
B	Buildings	17,351
C	Structural Steel	303,338
D	Ductwork	522,751
E	Tanks	29,798
F	Storage Bins	22,138
G	Pumps	86,938
H	Fans	151,973
I	Machinery	1,826
J	Material Handling Equipment	261,053
K	Special Equipment	462,102
L	Insulation	52,578
M	Piping	271,960
N	Instruments	166,838
O	Electrical	153,581
P	Painting	28,942
Q	Sitework	205,646
Sub Total		\$2,979,415
Site clearance and preparation)		
Initial MgO charge, etc.)		655,585
Total System Cost		\$3,635,000

*Includes Engineering Cost

TABLE 36

10.1.2 System Cost Details

Regeneration Plant and Acid Plant
Modifications

Chemico		
<u>Cost Code</u>	<u>Description</u>	<u>Cost *</u>
A	Foundations	\$ 176,942
B	Buildings	57,342
C	Structural Steel	166,342
D	Ductwork	24,774
E	Heat Exchangers	40,803
F	Tower	6,611
G	Tanks	16,888
I	Storage Bins	52,487
J	Pumps	13,579
K	Fans	38,096
O	Material Handling Equipment	86,743
P	Dust Collection	9,970
R	Calciner	584,811
S	Insulation	44,447
T	Piping	424,791
U	Instruments	72,994
V	Electrical	179,433
W	Catalyst	1,926
X	Painting	23,018
Y	Sitework	55,357
Z	Leasing	216,866
Total		\$2,294,220

* Includes Engineering Costs

10.2 OPERATING COSTS

Operating costs for the F.G.D. installation at Mystic Station are shown in Table 37. These costs are separated to show expenses for operating labor, utilities and maintenance as well as costs that can be identified as specific to the test program. A further separation is provided to show the costs incurred during the three principal periods of the test program.

Similar information is shown in Table 36 for the regeneration section. Included in this table is the expense for maintaining the laboratory and testing facilities at both sites and field administration costs. Because modifications and maintenance of the calciner and material handling equipment constitutes the largest percentage of the maintenance costs these areas have been identified separately in this section.

Table 37 presents the project management cost details as a separate item. Almost all of these costs are specific to operation of a prototype system, administration of the test and development effort, data handling and report preparation.

10.3 PROCESS ECONOMICS

The program described in this report combined elements of process development and pilot plant work with normal start-up procedures for the prototype system. Similarly, maintenance work on the unit was often in the form of modifications to pieces of its equipment. Because of these aspects, it is not possible to determine operating costs directly from the data. Instead, the information contained in this section has been combined with the observations and findings of the program to provide guidelines for establishing specifications for future plants and required quantities of materials for plant operations.

A source of data on process economics for the MgO slurry F.G.D. System is the Environmental Protection Agency Report, "Conceptual Design and Cost Study-Sulfur Oxide Removal from Power Plant Stack Gas-Magnesia Scrubbing-Regeneration" (10) which presents economics for a variety of plant sizes and configurations.

10.2.1

Operating & Maintenance Cost Details
F.G.D. System - Boston Edison Co.

TABLE 37

	Pre-Startup Thru Break-In Period	Planned Operational Testing	Continuous Operations	Project Termination	Total
Operations					
Labor* (Incl. Supv.)	\$232,324	\$212,169	\$115,408		\$ 559,901
Electricity	26,421	33,195	45,743		105,359
Fuel Oil (for dryer)	13,806	15,980	25,024		54,810
Water	3,476	3,958	4,740		12,174
Steam	6,858	2,599	2,756		12,213
Maintenance					
Labor*	134,090	180,955	59,881		374,926
Supplies	67,842	55,213	52,742		175,797
Spare Parts*	- 0 -	50,947	- 0 -		50,947
Subtotal O&M	484,817	555,016	306,294		1,346,127
Test Program Costs					
Training Program*	6,401				6,401
Cleanup*	82,373	64,402	19,822		166,597
Subtotal Test Program	88,774	64,402	19,822		172,998
Termination & Mothballing Costs*				\$89,843	89,843
TOTAL F.G.D. SYSTEM COSTS	\$573,591	\$619,418	\$326,116	\$89,843	\$1,608,968

*Incl. 50% General Overhead or Mark-Up

Regeneration Plant Operations Cost Details
Including Maintenance & Modification Plus
Testing and Quality Control Program

TABLE 3B

	Pre-Startup Thru Break-In Period	Planned Operational Period	Continuous Operations	Total
<u>Administrative Costs</u>				
Field Office (1)	\$ 53,262	\$33,466	\$16,512	\$102,240
Field Transportation (Boston & Rumford)	9,400	3,200	1,000	9,600
Home Office				
Salaries (Incl. Overhead)	41,649	33,893	13,019	88,561
Miscellaneous (Incl. Communication & Reproduction)	2,712	6,016	2,756	11,480
Payroll Taxes & Insurance	4,970	3,890	1,992	10,852
Travel & Living Expense	3,928	3,435	2,486	9,849
Subtotal Administration	\$110,924	\$83,900	\$37,761	\$232,585
(1) Includes Salary & Overhead for Field Accountant				
<u>Operations Costs</u>				
Essex Chemical Leasing Fees	152,372 ⁽²⁾	72,398	55,600	280,370
Operating Costs				
Operating Labor (Incl. Overhead)	98,297	60,300	37,704	196,301
Downtime	468	363	144	995

TABLE 38
(Continued)

	Pre-Startup Thru Break-In Period	Planned Operational Period	Continuous Operations	Total
Utility Costs				
Fuel Oil	22,081	23,914	30,814	76,809
Cooling Water	2,538	2,983	2,046	7,568
Electricity	21,508	15,386	10,951	47,845
Operating Chemicals (3)				
MgO (makeup)	47,629	64,152	41,073	152,854
Coke	5,430	5,827	2,192	13,449
Other Chemicals	1,474	904	3,294(4)	5,672
Transportation (MgO & MgSO ₃)	13,807	25,964	23,017	62,788
Subtotal Operations	\$365,604	\$272,211	\$206,835	\$844,651
(2) Includes leasing costs from 10/71				
(3) Includes freight				
(4) Includes \$2,928 caustic for tail gas scrubber system				
Maintenance Costs				
Spare Parts	21,354			21,354
Plant Maintenance Labor	30,631	9,238	3,654	43,523
Essex Supplied Material	17,153	2,483	3,731	23,347
Outside Maintenance (5)				
Routine Maintenance & Supplies	21,557	23,066	8,061	52,684
Code O Bins/Mat'l Handling/Pulverizer	13,259	17,676	13,369	44,304
Code R Calciner Modifications	13,271	11,292	6,404	30,967

10. 2. 2 (Cont'd)

TABLE 38
(Continued)

	Pre-Startup Thru Break-In Period	Planned Operational Period	Continuous Operations	Total
Miscellaneous Tools & Supplies	8,504	6,913	4,631	20,048
Subtotal Maintenance	\$125,709	\$ 70,668	\$ 39,850	\$ 236,227
(5) Includes Subcontract Labor & Shipping Costs				
Quality Control & Testing Costs				
Salaries (Incl. Supervision & Overhead)				
F. G. D. Plant at Mystic Station	983	55,218	41,298	97,499
Regeneration Plant	131,807	69,799	39,709	241,315
Material and Supplies	11,660	5,531	10,974	28,315
Laboratory Trailer (F. G. D. Plant)	1,030	1,030	734	2,794
Special Test Work				
Stack Analyses (F. G. D. Plant)		20,359		20,359
Spectrometric Characterization			11,682	11,682
Metallurgical Testing			2,720	2,720
Subtotal	\$145,480	\$151,937	\$107,117	\$ 404,534
TOTAL REGENERATION PLANT COSTS	\$747,717	\$578,716	\$391,564	\$1,717,997

TABLE 39

10. 2. 3 Project Management Cost Details

	Pre-Startup Thru Break-In Period	Planned Operational Testing	Continuous Operation	Project Termination	Total
Direct Salaries					
Field Costs, (Incl. Operating Supvr.) ⁽¹⁾	\$106,212	\$ 84,265	\$43,520	\$ -0-	\$233,997
Home Office, (Incl. Engineering) ⁽¹⁾	275,732	117,190	25,978	34,582	453,482
Outside Engineering & Inspection	33,360	11,156	799		45,315
Miscellaneous (Incl. communication & Reproduction)	13,239	15,121	9,895		38,255
Payroll Taxes & Insurance	10,297	5,436	2,925		18,658
Travel & Living Expense	50,032	27,632	11,463		89,127
TOTAL PROJECT MANAGEMENT	\$488,872	\$260,800	\$94,580	\$34,582	\$878,834

⁽¹⁾ Includes Overhead

In order to apply the findings of this study to improving economic predictions for the magnesia slurry F. G. D. process, a comparison of costs is made for one case presented in the "Conceptual Design and Cost Study" using costs developed from the guidelines resulting from this work.

The case chosen is a Magnesia Slurry Absorption-Regeneration System for a 200 MW, coal fired unit, 3.5% S in fuel and a 150 TPD sulfuric acid plant. (11) An advantage of this case is that it integrates all of the facilities from the boiler to the acid plant at a single site which eliminates the uncertainty associated with estimating transportation and storage costs.

Following are some of the significant aspects used in developing the manufacturing costs:

A. Delivered Raw Material - Measurement of system losses during the controlled run indicate an MgO makeup rate equal to 5% of the feed is reasonable.

B. Conversion Costs - Labor- Successful operation of the F. G. D. System was attained with the assignment of one control operator and one auxiliary operator per shift. It should be noted that this staff could handle two trains of equipment. Regeneration plant and acid plant operation is accomplished with two operators plus one roving operator per shift.

Utilities - Fuel Oil - The higher fuel consumption of the dryer in the study was related to the reduced efficiency caused by the modification noted. Future installations would employ properly designed dryers, therefore fuel consumption can be estimated by conventional methods. No provision is made for reheat as no separate reheat was used in the prototype operation.

Steam - MgO slaking at 180°F is provided by direct steam sparging.

C. Maintenance - Despite the high costs normally associated with maintenance and modifications of a prototype system, actual maintenance costs incurred were only $5\frac{1}{4}\%$ of erected value for the F. G. D. unit and $4\text{-}3/4\%$ for the regeneration plant. Using this basis, a 5% maintenance charge appears conservative.

D. Analysis - Reliance on wet chemical methods for critical control characteristics of the F. G. D. and regeneration system plus the normal requirements of the acid plant mandate close analytical support. One chemist per shift plus supervision and supplies are included.

Table 40 summarizes the fixed investment costs using the format developed in the E. P. A. study. In both cases the design parameters are as follows:

200 MW coal fired unit	
$3\frac{1}{2}\%$ sulfur in the coal	
SO ₂ removal	90%
Plant on stream time	80%
Coal consumption	554,200 T/Yr.
Heat rate	9,500 BTU/kwh

The E. P. A. study noted the inclusion of stack reheat by steam to 175°F though no costs were included for operation. No reheat is included in our comparison as the prototype plant did not employ reheat.

Table 41 summarizes the manufacturing costs, again using the E. P. A. format. It should be noted that only the direct costs are listed, no allowance is made for revenue from the sale of sulfuric acid or for depreciation and other indirect costs as these will vary from the viewpoint of either the utility or chemical manufacturer.

Other arrangements for processing the products from this F. G. D. system have been proposed. In one of these a tariff is paid by the power plant to an acid manufacturer to regenerate the absorbent. A study* of the plan, based on a \$15/ton differential cost between high and low sulfur coal, has shown a saving to the utility of 1.6 mills/kwh while paying a processing fee sufficient to provide a 25% before-tax return on investment to the chemical company. Similar economics obtain for a fuel oil fired power plant at a \$3/bbl differential between high and low sulfur fuel.

* Additional information is presented in the E. P. A. Capsule Report on Magnesia Scrubbing (EPA 625/2-75-007).

TABLE 40

SUMMARY OF ESTIMATED FIXED INVESTMENT
MAGNESIA SLURRY SCRUBBING-REGENERATION PROCESS
(200-MW New Coal-Fired Power Unit, 3.5th S in Fuel; 150 TPD H₂SO₄)

	From EPA Cost Study Investment, \$ (1)	From This Study Investment, \$ (2)
Land, site clearance, excavation, landscaping, roads, railways, walkways	200,000	-0-
Particulate scrubbers (2 scrubbers with surge tanks, agitators, pumps, and fly ash neutralization and disposal facilities)	1,445,000	3,790,000
Sulfur dioxide scrubbers (2 scrubbers with surge tanks, agitators, pumps, mist eliminators and fans)	1,602,000	4,360,000
Optional bypass duct around scrubbers	209,000	-0-
Slurry processing (screens, tanks, pumps, agitators and heating coils, purification facilities, centrifuges, and conveyors)	416,000	(2,510,000)
Drying (drying system, dust collectors, conveyors and MgSO ₃ storage hopper)	470,000	(
Calcining (calcining system, fans, MgO and coke storage hoppers, feeders, conveyors, elevators, waste heat boiler, dust collectors)	635,000	1,830,000
Magnesium oxide slurrying (MgO unloading and storage facilities, feeders, conveyors, elevators, slurry tank, agitator, and pumps)	140,000	410,000
Sulfuric acid plant (complete contact unit for sulfuric acid production, dry gas purification system)	1,495,000 (3)	4,500,000 (4)
Sulfuric acid storage (storage and shipping facilities for 30 days production of H ₂ SO ₄)	108,000	-0-
Fuel oil storage (fuel oil storage and distribution system including storage tank, hold tanks, heat exchanger, transfer and feed pumps)	94,000	-0-
Control room building, including motor controls, laboratory, and lockers	150,000	Included Above
Service facilities and buildings all location for maintenance, shops, and offices	410,000	-0-
Subtotal direct investment	7,374,000	17,400,000
Engineering design and supervision	664,000	(
Construction expense	811,000	(Included Above
Contractor fees	442,000	(
Contingency	959,000	(
Subtotal fixed capital investment	10,250,000	17,400,000
Allowance for startup and modifications	1,025,000	Included Above
Interest during construction (6.00 percent rate)	410,000	-0-
Total fixed capital investment	11,685,000	17,400,000

(1) 1972 Costs

(2) 1975 Costs

(3) "Dry" Sulfuric Acid Plant & Tail-Gas Scrubber

(4) Double Absorption Sulfuric Acid Plant

TABLE 41
ANNUAL MANUFACTURING COSTS FOR 25% H₂SO₄ FROM SCRUBBED POWER PLANT STACK GAS
MAGNESIA SLURRY SCRUBBING-REGENERATION
200-MW Existing Coal-Fired Power Unit, 3, 5% S in Fuel

	From EPA Cost Study (10)			From This Study		
	Annual Quantity	Unit Cost \$	Total Annual Cost \$	Annual Quantity	Unit Cost \$	Total Annual Cost \$
Delivered raw material						
Lime	56.5 tons	16.00/ton	900	-0-		-0-
Magnesium oxide (98%)	463 tons	102.40/ton	47,400	875 tons	150/ton	131,250
Coke	322 tons	23.50/ton	7,560	450 tons	80/ton	36,000
Catalyst	760 liters	1.51/liter	1,140	2,700 liters	1.25/liter	3,375
Sub-Total raw material			57,600			170,625
Conversion Costs						
Operating labor and supervision	30,440 man-hr	6.00/mh	182,800	50,000 man-hr	8.00/mh	400,000
Utilities						
Fuel Oil	3,166,000 gal	0.09/gal	284,900	9,800,000 gal	0.298/gal	2,941,200
Steam	22 MM lb	0.60/MM lb	-	4MM lb	2/MM lb	8,000
Heat Credit	8,600 MM Btu	0.46/MM Btu	43,400	-0-		-0-
Process Water	931 MM gal	0.65/MM gal	46,500	403 MM gal	0.25/MM gal	100,000
Electricity	28.2 MM kWh	0.007/kWh	197,300	34 MM kWh	0.01/kWh	340,000
Maintenance Labor and Material, .07 x \$13,083,000			915,800	.05 x \$17,400,000		870,000
Analyses			45,000			100,000
Sub-Total conversion costs			1,668,800			2,679,220
Total direct costs			1,725,800			2,833,045

Note: Direct cost 2 mills/kwh (at 0% rating)
8c/lb of sulfur removed

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13. CONVERSION FROM ENGLISH TO METRIC UNITS

<u>To Convert from</u>	<u>To</u>	<u>Multiply by</u>
atmosphere (normal)	bar	1.01325
atmosphere (normal)	pascal	101,325
barrel (42 US gallons)	meter ³	0.15899
British thermal unit (Btu)	joule	1055.1
Btu/hour	watt	0.29307
Btu/pound mass	joules/gram	2.32600
Btu/pound mass - °F	joules/gram - °K	4.18680
foot	meter	0.30480
foot ²	meter ²	0.09290
foot ³	meter ³	0.02832
foot ³ /minute	meter ³ /minute	0.02832
foot-pound force	joule	1.35582
gallon (US)	meter ³	0.00379
gallon (US)/minute	meter ³ /hour	0.22712
grain	milligram	64.7989
horsepower	kilowatt	0.74570
inch	centimeter	2.5400
inch H ₂ O (60°F)	kilopascal	0.24884
pound force	newton	4.44822
pound mass av	kilogram	0.45359
pound mass av	metric ton (tonne)	0.0004536
pound force/inch ²	kilopascal	6.89476
pound mass/foot ³	kilograms/meter ³	16.0185
°Rankine	°Kelvin	0.55556
ton mass (US short)	kilogram	907.185
ton mass (US long)	kilogram	1016.05

APPENDIX "A"

MAGNESIUM SULFITE HYDRATES TRANSITION & FORMATION

Process considerations are given to the existence of the two hydrates of MgSO_3 which have differing physico-chemical properties as the absorption processes are normally operated near the transition temperature region for these hydrates.

$\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ - $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ Transition

It has been observed (6) that the transition of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ to $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ at 40°C (104°F) is negligible. A measurable, although still slow transition can be observed at 65° (149°F) and at 70°C (158°F) the transition is completed in 10 hours.

Further studies (7) indicated that at 15°C (59°F) and at 35°C (95°F) no transformation of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ to $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ occurred. Also in this work, the concentration of MgSO_4 in solution was varied from 0 to 30%. With high MgSO_4 concentration in the solution the sulfite crystals were highly contaminated (to the extent of 40%) MgSO_4 . At 55°C (141°F) and at 75°C (167°F) rapid transformation of the hexahydrate to trihydrate occurred. These authors were of the opinion that MgSO_4 solutions aid in the transformation of hexahydrate to trihydrate.

Since the temperature of the absorber at Boston is 135°F and no such rapid transformation of the hydrates was observed, a study of the transition of the two hydrates was undertaken using the following procedure:

Slurries were prepared with a composition similar to that obtained in normal operation and were placed in glass-stoppered bottles. The bottles were placed in a constant temperature bath. After a predetermined period of time the bottles were taken out and the contents filtered immediately, washed with methanol and dried in air and at 40°C. The crystals were analyzed for sulfite, sulfate, and MgO content.

The ratio of the two hydrates in the crystals was analyzed using a chemical method developed at Chemico's laboratory. This method is discussed in Appendix C, Analytical Techniques.

RESULTS

At room temperature (in contact with water) the trihydrate is converted to the hexahydrate. This transformation also takes place in 8% MgSO_4 solution. But when the concentration of MgSO_4 in solution reaches 15% or above, no further transition to hexahydrate occurs. In this transition the crystal size of the resultant hexahydrate becomes 8 to 10 fold larger than the original trihydrate crystals tending to support the hypothesis that the crystals first dissolve in the solvent and then crystallize out in the other form. In contrast to the trihydrate, the hexahydrate appeared to change over to the trihydrate with the rise in concentration of MgSO_4 in solution. However, conflicting results were obtained in this study and, consequently, no firm conclusions could be drawn. Table A-1 summarizes the room temperature data.

In our study, no transition of the hexahydrate to trihydrate was observed at 135°F (57°C), even after 48 hours, nor was the catalytic effect of MgSO_4 claimed by Kovachev and others observed. The transition temperature of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ to $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ appears to be a few degrees above 135°F and most probably at 138°F. The pH of the medium seems to have some effect on the rate of transition of the hydrates. It appears (Table A-2) that alkaline pH retards while acid pH favors the rate of transition. In summary, the major factor in the transition of the hexahydrate to trihydrate appears to be temperature. The transition temperature is 138°F (59°C). MgSO_4 does not appear to play a significant role in the transition. On the other hand, pH and presence of trihydrate do have some effect on the rate and temperature of transition.

Table A-1

MAGNESIUM SULFITE
HYDRATE TRANSITION AT ROOM TEMPERATURE

<u>Conditions for Digestion</u>	<u>Trihydrate</u>	<u>Hexahydrate</u>
1. In 8% MgSO_4 solution for 24 hrs.	All Hexahydrate	No change
2. In 15% MgSO_4		
a. 20 Hrs.	No Change	Mostly hexa with some trihydrate
b. 64 Hrs.	No Change	40% $6\text{H}_2\text{O}$ 60% $3\text{H}_2\text{O}$
c. 97 Hrs.		No change
3. In 20% MgSO_4		
a. 20 Hrs.	No Change	80% $6\text{H}_2\text{O}$ 20% $3\text{H}_2\text{O}$
b. 64 Hrs.	No Change	40% $6\text{H}_2\text{O}$ 60% $3\text{H}_2\text{O}$
c. 72 Hrs.	-	No change
d. 97 Hrs.	-	No change

TABLE A-2
TRANSITION OF $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$
pH ADJUSTED BY DIL. H_2SO_4

<u>Conditions for Digestion</u>	<u>Results</u>
1. pH 7.00: 138°F. 45 mins. in water	All trihydrate
2. pH 7.00: 135°F. 45 mins. in water	Hexahydrate with few percent Trihydrate
3. pH 7.10: 140-146°F. 45 mins. in water	All trihydrate
4. pH 7.00: 134-135°F. 45 mins.; 15% MgSO_4	All hexahydrate
5. pH 7.00: 132-134°F. 45 mins. in water	All hexahydrate
6. pH 7.15: 134-136°F. 45 mins. in water	All trihydrate
7. pH 7.40: 138-141°F. 45 mins. in water	A little trihydrate 10%: 90% Hexahydrate

Magnesium Sulfite Hydrate Formation

Magnesium sulfite trihydrate ($\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$) is formed in the prototype FGD system after equilibrium is attained. Laboratory studies were undertaken in an effort to determine the conditions which led to the formation of each of the hydrates and the influence of the systems components on crystal type. These experiments including the effort to simulate the reaction occurring in the venturi absorber, were unsuccessful in duplicating the hydrate formed in the prototype system.

Two experimental conditions were used: a) SO_2 at room temperature was reacted with MgO slurry in (i) water and in (ii) MgSO_4 solution at 135°F and at a pH of 6.8 to 7.20; b) SO_2 at 300°F was reacted with MgO slurry in water at 135°F ; and a pH of 6.80 to 7.20. The reaction period in both cases was of 75 minutes and SO_2 gas (pure) at a rate of 200 ml./min. and air at a rate of 3 liters/minute were added through a glass T-tube connected to a Vycortube wrapped with heating tape.

The gas was bubbled through 400 ml. of water containing 1-2 gm. of MgO maintained at a temperature of 135°F in a 600 ml. beaker. The temperature of the reaction-beaker was controlled at 135°F by a water-bath.

The pH of the reaction medium was kept at 6.8-7.2 by controlled addition of MgO slurry (10% in water). The whole reaction lasted 75 minutes.

After reaction the slurry was filtered and the coke and filter analyzed. In all cases the exclusive product was $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ as shown in Table A-3.

TABLE A-3

REACTION OF SO₂ with MgO

Slurry Temp. (°F)	Slurry pH	MgSO ₄ (%)	SO ₂ Temp. (°F)	Reaction Products		Composition %	
				Filtrate %MgSO ₄	Cake MgSO ₃ Hydrate	MgSO ₃	MgSO ₄
130-136	6.8 - 7.2	0	Amb.	0.43	Hexahydrate	48.6	0.2
130-136	6.8 - 7.2	15%	Amb.	12.1	Hexahydrate	46.4	1.9
135	6.8 - 7.2	0	300°	0.5	Hexahydrate	47.9	0.3
135	6.8 - 7.2	0.5	300°	1.4	Hexahydrate	48.8	1.0
135	6.8 - 7.2	1.4	300°	1.3	Hexahydrate	48.3	0.6
							1.2

APPENDIX B

PHYSICO-CHEMICAL DATA

It is well known that magnesium sulfite exists in two forms: $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$. A third form ($\text{MgSO}_3 \cdot \text{H}_2\text{O}$) has been reported but no evidence of its existence has been found in this study.

X-RAY CRYSTALLOGRAPHIC DATA

X-ray crystallographic study of samples submitted for analyses showed the hexahydrate is rhombohedral with space group $R\bar{3}$, with three molecules per unit cell with the following dimensions:

$$a = 8.820 \text{ \AA}$$

$$c = 9.052 \text{ \AA}$$

The calculated density is 1.724 gm./ml. while the measured value is 1.730 gm./ml.

The trihydrate is orthorhombic with space group Pbn_2 . There are four molecules per unit cell: a, 9.36; b, 9.45; and c, 5.51 $\text{\AA}$. The calculated and measured densities are 2.138 gm./ml. and 2.180, respectively.

The major X-ray spectra for the hydrates are given in Table B-1.

IR & RAMAN SPECTRAL DATA

<u>Laser Raman Spectrum (Solid) in CM^{-1}</u>	
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$	$\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$
962 (s))	967.7 (s) triplet
) doublet	
944 (s))	477 (m) with shoulder
482 (m)	

The laser used was Argon excitation at $4880 \text{ \AA}$ with scanning from 200 cm^{-1} to 1400 cm^{-1} . (Because of low solubility in water no sharp spectrum could be obtained in aqueous medium).

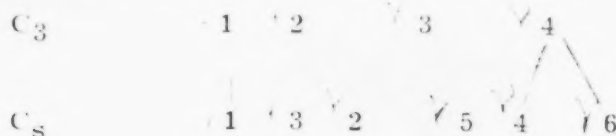
The infrared study of the two hydrates of MgSO_3 was conducted in: KBr pellet, nujol mull, as well as MIR with KRS-5 plate. IR spectra of the two hydrates vs. temperature were also studied and an attempt was made to correlate the high temperature IR spectra with a DTA study of the two hydrates.

ROOM TEMPERATURE SPECTRA OF THE HYDRATES
IN THE SOLID STATE (KBr PELLET) IN cm^{-1}

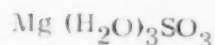
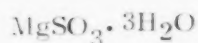
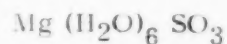
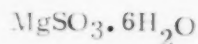
<u>Assignment</u>	<u>Na_2SO_3</u>	<u>$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$</u>	<u>$\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$</u>
1	1010	950 (s)	950 (s)
2	633	640 (m)	900 (s)
3	941	925 (s)	640 (m, sh)
4	496	490 (w)	400 (m)
5			450 (w)
6			850 (ms)
			320 (ms)
		700 (m)	700 (s)
		260 (ms)	260 (w)

The 700 cm^{-1} band in $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and in $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ is assigned to coordinated water.

From the IR spectrum it appears that the sulfite ion in the hexahydrate has C_3 symmetry while in the trihydrate this symmetry is lowered to C_s . The correlation between the two are as follows:

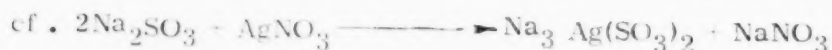
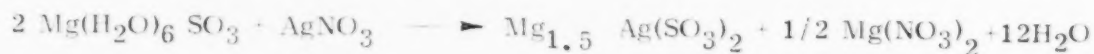


From the IR data, as also from chemical reactions and DTA work, two hydrates can be represented structurally as follows:



The two hydrates can be easily distinguished from their IR spectrum by the 320 cm^{-1} , 450 cm^{-1} , and 850 cm^{-1} , bands. Also, in the hexahydrate the 700 and 640 cm^{-1} bands appear as a doublet, but in the trihydrate only the 700 cm^{-1} band is pronounced. The presence of more bands in the trihydrate spectrum than expected is probably due to the coordination and crystal field effects.

The previous representation of the two hydrates is also supported by their reactions with $AgNO_3$ solutions: (The difference in reaction of the two hydrates was discovered during this work and used as a method of analysis for them)



showing that the SO_3^{-2} ion is present in the hexahydrate as a salt-like ion.

With the trihydrate the reaction is:



Because of the presence of SO_3^{-2} inside the coordination sphere and the low ionisation constant of such complexes, the concentration of SO_3^{-2} ion in solution is too low to form complexes with Ag^+ and only the insoluble Ag_2SO_3 salt is formed.

DTA of the hexahydrate shows two prominent endotherms - one at 130°C , and the other at 240°C , while the trihydrate gives only one endotherm at 240°C .

The two hydrates were heated at 130°C and 160°C , for extended periods of time (24 hours or more) in an oven. The results are as follows:

<u>Temperature $^\circ\text{C}$</u>	<u>Tri-</u>	<u>Hexa-</u>
130 $^\circ\text{C}$ for 7 days	Wt. loss 24% Composition $\text{MgSO}_3 \cdot \text{H}_2\text{O}$	Wt. loss 44% Composition $\text{MgSO}_3 \cdot \text{H}_2\text{O}$
160 $^\circ\text{C}$ for 94 hrs.	Wt. loss 29.5% Composition $\text{MgSO}_3 \cdot 0.5\text{H}_2\text{O}$	Wt. loss 47% Composition $\text{MgSO}_3 \cdot 0.5\text{H}_2\text{O}$

IR spectrum of the two hydrates (Table B-2) were taken while being heated at 130°C and 160°C in a heated cell. After 24 hours of heating the two hydrates gave essentially identical spectrum for the same heating temperature. The 160°C spectrum contained bands due to sulfate ion present in a complex environment. This suggests that at least up to 160°C the SO_3^{-2} ion in the trihydrate is still present inside the coordination sphere. As for the hexahydrate, at about 130°C the SO_3^{-2} ion enters the coordination sphere displacing water and remains there at least up to 160°C , at which temperature partial oxidation of sulfite ion takes place.

PHYSICAL PROPERTIES

The specific gravities of the two hydrates were measured with a pycnometer, in 2-methyl butanol, in which neither of the hydrates dissolve.

<u>Hydrate</u>	<u>Sp. Gravity</u>
Magnesium Sulfite Hexahydrate	1.730 gm./ml.
Magnesium Sulfite Trihydrate	2.18 gm./ml.

The solubility of the two hydrates in water was also found to be different:

<u>Hydrate</u>	<u>%MgSO₃ In Water</u>	<u>g./liter</u>
Magnesium Sulfite Hexahydrate	0.42	8.56
Magnesium Sulfite Trihydrate	0.76	11.55

Additional data is given in Table B-3.

The solubility of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ increases with the rise in concentration of MgSO_4 in solution as well as with temperature.

SOLUBILITY OF $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ in MgSO_4 SOLUTION

<u>Conc. of MgSO_4 in Soln. (as %)</u>	<u>MgSO_3 (in gm./liter)</u>
5	7.5
10	8.5
15	9.0
20	9.20
25	8.90

NOTE: At 25% MgSO_4 solution the solubility starts to decrease.

SOLUBILITY OF THE HEXAHYDRATE IN WATER AND
IN 25% MgSO_4 SOLUTION vs. TEMPERATURE

<u>Temperature °F</u>	<u>% MgSO_3 in</u>	
	<u>Water</u>	<u>25% MgSO_4</u>
70	0.75	0.94
110	0.99	1.43
135	1.42	2.63
180	1.75	5.99

(Since at 180°F the hexahydrate changes over to trihydrate, the solubilities at 180°F are probably those of the trihydrate).

SOLUBILITY OF THE TWO HYDRATES IN MgSO_4 SOLUTION

<u>% MgSO_4</u>	<u>% MgSO_3 in Solution</u>	
	<u>Tri-</u>	<u>Hexa-</u>
15	1.22	1.02
25	1.14	0.94

TABLE B-1
X-RAY CRYSTALLOGRAPHIC DATA

$\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$	$d(\text{\AA})$	3.35	6.71	4.27	6.71
	I/I_0	100	80	60	80
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$	d	3.87	2.74	4.40	5.7
	I/I_0	100	100	80	4

TABLE B-2

IR SPECTRA OF THE HYDRATES AT HIGH TEMPERATURE

<u>Temperature (°C)</u>	<u>Hexahydrate</u>	<u>Trihydrate</u>
130°	990)) (s) 960) triplet) 900)	950 (s) (broad)
	690 (m)	690 (m)
	400 (w)	400 (w)
	320 (s)	350 (sh)
		320 (m)
	260 (w)	260 (vw)
160°	1050 (m)	1050 (m)
	900 (s)	900 (s)
	700 (m)	700 (m)
	670 (m)	640 (m)
	390 (m)	390 (m)
		300 (w)
	<u>Ionic SO₄⁻²</u>	<u>Complex SO₄⁻²</u>
	1104 (vs)	1032 - 1044 (s)
	613 (s)	1117 - 1143 (s)
		970 (m)
		645 (s)
		604 (s)
		438 (m)
<u>Band Intensity</u>		
s - strong		
m - medium		
w - weak		
vw - very weak		

TABLE B-3
SOLUBILITY IN H₂O

MgSO ₃ ·6H ₂ O			MgSO ₃ ·3H ₂ O		
Temp. °C		% MgSO ₃	Temp. °C		% MgSO ₃
(32°F)	0	0.338	(100.4 °F)	38	1.034
(59°F)	15	0.497	(107.6 °F)	42	0.937
(77°F)	25	0.646	(122 °F)	50	0.844
(95°F)	35	0.846	(131 °F)	55	0.817
(113°F)	45	1.116	(144 °F)	62.5	0.748
(131°F)	55	1.456	(167 °F)	75	0.664
(144°F)	62.5	1.95	(185 °F)	85	0.623
			(203 °F)	95	0.615

APPENDIX C

ANALYTICAL TECHNIQUES FOR MAGNESIA MATERIAL

A. MgO is analyzed by acid-base titration.

1. Reagents

- (a) Standard sulfuric acid 0.5N. Reagent grade acid is diluted as: 1 ml. of acid is added to 71 ml. of distilled water. Concentration checked by titrating against standard alkali.
- (b) Standard NaOH 0.5N solution. Dissolve 20 gm. of reagent grade alkali in a liter of distilled water. Concentration is checked by titrating against standard potassium hydrogen phthalate.
- (c) Potassium hydrogen phthalate (0.1N solution). Dissolve 20.4230 gm. of reagent grade salt in 1 liter of distilled water.
- (d) Indicator (mixed). Dissolve 1.25 gm. of methyl red and 0.825 gm. of methylene blue in 1 liter of 95% alcohol. The indicator is pink in acid and green in alkaline solution. It is colorless or gray in neutral media. Use 10 drops for each titration.

2. Apparatus

- (a) Two 50 ml. automatic burettes attached to plastic bottles of 15 to 20 liters capacity.
- (b) Beakers, 250 and 400 ml.
- (c) Pipettes, 25 and 50 ml.

- (d) Teflon coated stirring bars.
- (e) Analytical balance.
- (f) Magnetic stirrer.
- (g) Hot plate.
- (h) Weighing paper.

3. Standardization of Acid and Alkali

Transfer 50 ml. of standard potassium hydrogen phthalate solution into a 250 ml. beaker. Add 100 - 125 ml. distilled water and 10 drops of indicator. Put a magnetic stirring bar inside the beaker and place it on the stirrer and titrate with NaOH. End point is reached when the indicator changes from pink to green. Repeat the process.

Determine the normality of H_2SO_4 using NaOH as the standard. Take 25 ml. of H_2SO_4 and titrate against NaOH using the above procedure.

Calculation

Normality of $\text{KHC}_8\text{H}_4\text{O}_4$

$$\frac{\text{Sample Weight}}{20.4230} = N$$

Normality of NaOH

$$= \frac{50 \times \text{normality of } \text{KH}_4\text{C}_8\text{H}_4\text{O}_4}{\text{ml. of NaOH}}$$

$$= N (\text{alkali})$$

Normality of H_2SO_4

$$= \frac{25}{\text{ml. of NaOH} \times N \text{ alkali}} = N (\text{acid})$$

4. Percentage of MgO in the sample

Weigh accurately 1 gm. of sample for centrifuge cakes, dryer products and calciner feeds, but 0.25 gm. for calciner products, in a 400 ml. beaker. Add 150 - 200 ml. of distilled water and 5 - 10 ml. of 30% H_2O_2 . Heat and boil for one-half hour. To the hot solution (not boiling) add 50 ml. of standard 0.5N H_2SO_4 , heat for another one-half hour. Cool to room temperature and titrate with 0.5N NaOH using the above indicator.

Calculation

$$\% \text{ MgO} = \frac{2.02}{\text{sample weight}} (50 \times \text{normality of } \text{H}_2\text{SO}_4 - \text{ml. of alkali} \times \text{normality of alkali})$$

B. MgSO₃ in Samples

This is determined idiometrically.

Dissolve 25 gm. of KI in as little water as possible. Weigh about 12.70 gm. of iodine (AR) and dissolve completely in the KI solution. Any insoluble can be filtered through a glass Gooch crucible. Dilute the clear solution to a liter by distilled water. Store in a dark bottle.

Standardize the iodine solution as follows:

Weight accurately, as close as possible, 0.2 gm. of AR grade As_2O_3 in a beaker. Dissolve in the smallest amount of 40% NaOH solution. Dilute to 200 ml., add a drop of phenolphthalein indicator. Add, dropwise, 1:1 H_2SO_4 until the pink color disappears. Add about 5 gm. of NaHCO_3 to the solution, stir with a magnetic stirrer and titrate with 0.1N iodine solution with starch indicator.

Calculation

$$\frac{\text{Wt. of As}_2\text{O}_3 \text{ taken}}{0.04948} = A$$

$$\text{Normality of iodine} = \frac{A}{\text{ml. of I}_2 \text{ solution}}$$

1. 0.1N Na₂S₂O₃ solution:

Dissolve 25 gm. of Na₂S₂O₃·5H₂O per liter. Add 0.1 gm. of Borax per liter to stabilize the solution.

Sodium thiosulfate is standardized titrating against I₂ solution with starch as indicator. Take 25 ml. of Na₂S₂O₃ solution in a 250 ml. beaker, add 100 - 125 ml. of water and a few drops (10) of starch indicator. Titrate until the blue color persists for 1 minute.

Normality of Na₂S₂O₃ Solution

$$= \frac{\text{Normality of Iodine} \times \text{ml. of I}_2}{\text{ml. of Na}_2\text{S}_2\text{O}_3 \text{ Solution}}$$

2. Starch Indicator

Make a thin paste of about 9 gms. of soluble starch in cold water, then add it to one liter of boiling water with constant stirring. Boil for 2 to 3 minutes after all the starch has been added. Cool, add 2 ml. of Chloroform to preserve the solution.

3. Phenolphthalein Indicator

Dissolve 1 gm. of phenolphthalein in 50 ml. of alcohol and add 50 ml. of water. Filter off any insolubles.

Apparatus

1. A brown bottle (1 liter) fitted with a brown automatic burette (50 ml.).
2. An automatic burette attached to a $\text{Na}_2\text{S}_2\text{O}_3$ reservoir (10 - 15 liters).
3. Pipettes: 10, 25 and 50 ml.
4. Magnetic stirring bars.
5. Magnetic stirrer.

Procedure

Weigh out accurately about 0.25 gm. of the material. Add to a beaker containing 50 ml. of standardized iodine solution. Stir with a magnetic stirrer, add 10 ml. of 1:1 HCl and titrate immediately with standard sodium thiosulfate solution. Add 5 ml. of starch indicator to the beaker as soon as the color of the mixture becomes pale yellow. Continue titrating until the blue color disappears and the solution remains colorless for 30 seconds.

Calculation

$$\% \text{SO}_2 = \frac{3.22}{\text{sample weight}} \times (\text{ml. of I}_2 \text{ solution} \times \text{Normality} - \text{ml. of Na}_2\text{S}_2\text{O}_3 \text{ solution} \times \text{Normality})$$

$$\% \text{MgSO}_3 = \% \text{SO}_2 \times 1.625$$

C. Determination of MgSO₄

This is determined nephelometrically. A Hach colorimeter (DRA) was used for this determination.

Apparatus

1. Hach Colorimeter (DRA)
2. Pipettes: 1, 2, 5 and 10 ml.
3. Volumetric flasks.
4. Beakers.

Procedure

Weigh about 2.50 gm. of sample accurately in a beaker (250 ml.). Add 100 ml. of water and 25 ml. of 1:1 HCl. Boil for one-half hour. Filter off any insolubles. Dilute to 250 ml. in a volumetric flask.

Take appropriate volume (1, 2, or 5 ml.) in the bottle provided with the Colorimeter. Add the reagent supplied by Hach, dilute to mark and then read p.p.m. from the card in the Colorimeter. (The solution concentration is manipulated in such a way that p.p.m. reading is between 0 - 75).

Calculation

$$\% \text{ SO}_4 = \frac{\text{p.p.m.} \times \text{volume}}{\text{sample weight}} = A$$

$$\% \text{ MgSO}_4 = 1.253 \times A$$

- $\times$ = 0.05 for 5 ml. of the original solution
- = 0.10 for 2.5 ml. of the original solution
- = 0.125 for 2.0 ml. of the original solution
- = 0.25 for 1 ml. of the original solution

D. Carbon

Carbon in the sample is determined in Leco semiautomatic combustion furnace (#572-100). Follow the procedure described in the Leco instruction booklet.

E. Moisture Analysis

Two varieties of moisture are recognized in the centrifuge cakes:

(1) free or absorbed water

(2) combined or chemically bound water

1. Free or absorbed water:

Weigh out a beaker (250 ml.) and record weight. Add about 50 gm. of sample and record weight. Weigh a filter-paper and a clean watch-glass (large enough to accommodate the filter paper). Add approximately 70 ml. of acetone to the sample in the beaker and mix well. Transfer all the slurry (add more acetone if necessary) to the filter paper in a Buchner funnel, and filter under suction. Wash twice with acetone. Air-dry the sample. Transfer the paper to the watch-glass and dry in an oven at 40°C for one-half hour. Re-weigh the sample and watch-glass and filter paper to get the weight of the oven dried sample.

Calculation

$$\% \text{ Solid} = \frac{\text{Wt. of oven dried sample}}{\text{Wt. of original sample}} \times 100$$

$$\% \text{ Free water} = 100 - \% \text{ Solid}$$

2. Combined Water

Ground the oven dried sample in a mortar. Place sample (10 g.) on the aluminum pan of the Ohaus balance (#610). Adjust the wattage and the height of the lamp so that a temperature of 160 - 165°C is attained at the center of the pan. Heat for 50 minutes.

Calculation

% combined water = scale reading.

F. Other Analyses

1. Iron

Determined colorimetrically using Hatch. Follow the procedure given in water analysis Handbook by Hatch Chemical Company. For calculation and sample preparation: Weigh accurately about 1 g. of the sample. Transfer to a 250 ml. beaker, add 50 ml. water and 5 ml. of concentrated HCl. Boil for 15 minutes. Filter off insolubles and dilute to 1000 ml. Take suitable aliquots to give a reading of 2 p.p.m. or lower.

Calculation

$$\frac{\text{Reading in (p.p.m.)} \times 25}{\text{aliquot}} = \text{mgs. / 1000 ml.} = A$$

$$\frac{0.1 A}{\text{sample wt.}} = \% \text{ Fe}$$

Note: The pH of the iron solution should be between 3 and 6.

If too acidic, adjust pH by adding alkali.

2. Nickel

Weigh accurately about 1 gm. of sample in a 250 ml. beaker. Add concentrated HCl (10 ml.) and 100 ml. of water. Boil until solution is complete. Add 5 ml. of 30% H₂O₂ and boil for 15 minutes. Add NH₄Cl (2 gm.) and then add NH₄OH until it just smells of NH₃. Filter hot, wash the precipitate with hot water. Add a few drops of concentrated HCl until acid. To the hot solution add 25 to 50 ml. of dimethyl glyoxime solution and then 3 gms. of solid sodium acetate. Keep on low heat for at least 1 hour. Filter through a weighed No. 4 glass Gooch crucible - wash with hot water - dry at 110°C. for 1 hour - cool in a desiccator. Weigh. The difference in the two weights is the weight of Nickel dimethyl glyoxime complex.

$$\% \text{ Ni} = \frac{\text{Wt. of Ni-complex} \times 0.2031 \times 100}{\text{Wt. of sample taken}}$$

Dimethyl glyoxime solution

Dissolve 0.6 gm. of dimethyl glyoxime (solid) in 100 ml. of 95% ethyl alcohol. Filter if necessary.

3. Vanadium

Weigh accurately about 1 gm. of the sample in a 100 ml. beaker. Add 5 to 10 ml. of concentrated HCl, heat to dryness, cool, add 3 - 5 ml. of concentrated H₂SO₄ and heat again to dryness (fumes of SO₃). Cool. Add 50 ml. of water, boil for one-half hour. Filter, wash and dilute to 100 ml.

Take 10 ml. of the stock solution in a 100 ml. flask, add 5 ml. of 3% H_2O_2 and 0.25 g. of NaF. Make up to the mark with 2N H_2SO_4 . Transfer the solution to the cell and read absorption at 450 $\text{m}\mu$. Then determine the p.p.m. from the graph.

Calculation

$$\% \text{ V} = \frac{\text{p.p.m.} \times 0.1}{\text{sample wt.}}$$

NOTE: For 20 ml. of stock solution

$$\% \text{ V} = \frac{\text{p.p.m.} \times 0.05}{\text{sample wt.}}$$

Construction of graph

Weigh accurately analytical grade ammonium vanadate to make a stock solution of 1 mg. of V/ml. (1000 p.p.m.) in 5N H_2SO_4 . Make up solutions of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 p.p.m. vanadium content by proper dilution. Proceed as above and plot p.p.m. vs. absorbance curve.

4. Chloride

The chloride is determined by AgNO_3 titration.

Weigh accurately about 1 gm. of the sample in a 250 ml. beaker. Add 100 ml. of distilled water and 5 ml. of concentrated HNO_3 . Boil until the solution is reduced to half its original volume. Filter off any insolubles. Dilute to 200 ml. in a beaker or Erlenmeyer flask, add 5 ml. of 1:1 HNO_3 , 25 ml. of standard AgNO_3 , 1-2 ml. of ferric alum indicator and titrate with standard NH_4CNS solution until the reddish-brown color persists on stirring (use a magnetic stirring-bar during titration).

Calculation

ml. of $\text{AgNO}_3 \times N$ of AgNO_3 - ml. of $\text{NH}_4\text{CNS} \times N$ of $\text{NH}_4\text{CNS} = A$

$$\% \text{ Cl} = \frac{0.03546A}{\text{wt. of sample}} \times 100$$

For liquid samples use the above procedure. Take 25 to 100 ml. of liquid sample depending upon chloride content.

$$\text{mg. of Cl/liter} = \frac{35.46 A}{\text{vol. of sample taken}} \times 1000$$

Standard AgNO_3 Solution

Dissolve 16.9870 gm. of reagent grade AgNO_3 per liter. Store in a dark bottle away from direct light.

$$\text{Normality of } \text{AgNO}_3 = \frac{\text{Wt. of } \text{AgNO}_3 \text{ taken}}{16.9870}$$

Standard NH_4CNS Solution

Dissolve 7.6 gm. of NH_4CNS per liter. Standardize against AgNO_3 solution. Take 25 ml. of standard AgNO_3 solution in a 250 ml. beaker. Add 100 ml. of distilled water and 5 ml. of 1:1 HNO_3 . Add 1 ml. of ferric alum indicator and titrate to reddish-brown endpoint with NH_4CNS .

Calculation

$$\text{Normality of } \text{NH}_4 \text{ CNS} = \frac{25 \times \text{Normality of } \text{AgNO}_3}{\text{ml. of } \text{NH}_4\text{CNS}}$$

Ferric alum indicator

Dissolve 140 gm. of ferric ammonium sulfate (pure) in 400 ml. of water. Add 10 ml. of 6N HNO_3 (390 ml. of concentrated HNO_3 diluted to 1 liter). Heat if necessary. Filter off any insoluble. Cool. Dilute to 500 ml. with 6N HNO_3 .

5. Magnesium and Calcium by EDTA

Preparation of EDTA Solution

Dissolve 37.2240 gm. of reagent grade disodium dihydrate salt of EDTA in 1 liter of water - 0.1M EDTA. Standardize against AR CaCO_3 or Mg salt. Store in a plastic bottle.

$$\begin{aligned} 1 \text{ ml. of } 0.1\text{M EDTA} &= 2.4320 \text{ mg. of } \text{Mg}^{+2} \\ &= 4.0080 \text{ mg. of } \text{Ca}^{+2} \end{aligned}$$

Buffer

Dissolve 67.50 gm. of NH_4Cl in distilled water. Add 570 ml. of NH_4OH and dilute to 1 liter.

Indicator

Dissolve 0.5 gm. of Eriochrome Black T in 100 ml. of ethyl alcohol. Add 1 gm. of Murexide to 100 gm. of pure NaCl , mix well in a mortar. Store in a bottle.

Ammonium Sulfide Solution

Saturate 200 ml. of concentrated NH_4OH with H_2S (keep the solution cold while passing H_2S). Add 200 ml. of concentrated NH_4OH and dilute to 1 liter.

Standardization of EDTA using Ca^{+2}

Weigh any Ca compound (pure) accurately so that no more than 0.5 gm. of Ca^{+2} is present per liter.

Take 100 ml. of standard Ca^{+2} solution, add NaOH solution (4 gm. of NaOH per liter) until the solution has a pH 12 (check with pH paper). At this point precipitation might take place. Add a small amount of solid Murexide - NaCl indicator and titrate with EDTA to a color change of orange to violet.

Calculation

$$\text{Molality of EDTA} = \frac{\text{ml. of EDTA} \times \text{gm. of Ca}^{+2} \text{ in 100 ml.}}{0.04008}$$

Standardization of EDTA by Mg^{+2}

Weigh any AR grade Mg^{+2} salt accurately so that no more than 1 gm. of Mg^{+2} is present in 1000 ml.

To 100 ml. of nearly neutral solution add 10 ml. of buffer and 1 ml. of the Black T indicator and titrate from red to clear blue color.

$$1 \text{ ml. of } 0.1\text{M EDTA} = 0.002432 \text{ gm. } \text{Mg}^{+2}$$

Determination of Ca^{+2} and Mg^{+2} in centrifuge cake, dryer product, etc.

Weigh accurately 1.5 to 2 gm. of the sample in a 250 ml. beaker. Add 10 ml. of concentrated HCl and 10 ml. of water. Cover the beaker with a watch glass and heat (on low heat) almost to dryness. Add 100 - 150 ml. distilled water, boil until solution (a few ml. of concentrated HCl may be added). Add 5 gm. of NH_4Cl and NH_4OH dropwise until ammoniacal. Add 10 ml. of $(\text{NH}_4)_2\text{S}$ solution. Filter off any precipitate, wash with hot water and dilute to 1 liter.

Total Ca^{+2} and Mg^{+2}

For Mg^{+2}

To 25 ml. of the solution (almost neutral) add 5 ml. of buffer and 10 drops of Eriochrome Black T indicator. Titrate (with stirring) to blue endpoint. Note the ml. of EDTA used = 'A'.

For Ca^{+2}

To 25 ml. of stock solution add enough 1N NaOH until the pH of the solution reaches at least 12 (check with pH paper). Add 0.1 gm. of Murexide - NaCl

indicator. Titrate to violet end point with EDTA. Amount of EDTA consumed = 'B' ml.

Calculation

For Mg^{+2}

$$A - B = 'C' \text{ ml.}$$

Amount of Mg^{+2} in 25 ml,

$$= C \times \text{molality of EDTA} \times 0.02432$$

$$= C \text{ gm.}$$

$$\text{In 1000 ml.} = C \times 40 = C \text{ gm.}$$

$$\% Mg^{+2} = \frac{C}{\text{wt. of sample}} \times 100$$

For Ca^{+2}

Amount of Ca^{+2} in 25 ml,

$$= B \times \text{molality of EDTA} \times 0.04008 = b \text{ gm.}$$

Amount of Ca^{+2} in 1000 ml. = $b \times 40 = b \text{ gm.}$

$$\% Ca^{+2} = \frac{b}{\text{wt. of sample}} \times 100$$

6. Degree of Hydration of MgO

Determine the percentage of MgO in the sample using the procedure A.

Place sufficient amount of the sample in a beaker, add water to make a 10-15% slurry. Place the beaker inside an oil bath (set at the desired temperature level). Stir the contents of the beaker with a stirrer. Keep the beaker in the bath for the desired period of time. Filter under suction, wash the sample with acetone, dry in an oven at 45 - 50°C for 1 hour. Analyze again for MgO content by procedure A.

Calculation

% MgO in the sample before hydration = A

% MgO after hydration = B

% Hydration = (A - B) x 3.22

7. Determination of the Ratio of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ in the Centrifuge Cake

The two hydrates of magnesium sulfite behave differently towards silver nitrate solutions:

1 gm. of $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ = 2.1450 gm. of AgNO_3

1 gm. of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ = 0.4000 gm. of AgNO_3

Reagents

1. 0.5N AgNO_3 solution
2. 0.1N NH_4CNS solution
3. Ferric alum indicator

Procedure

Analyze the cake for H_2O , MgO , MgSO_4 and MgSO_3 contents in the usual way.

(a) amount of MgSO_4 less than 5%

and

(b) amount of MgSO_4 more than 5%.

For (a) no treatment is necessary.

For (b) add about 3 gm. of powdered centrifuge cake

to 200 ml. of absolute alcohol while stirring. Stir for one-half hour, filter under suction, wash with acetone and dry in air. Repeat the process until the amount of MgSO_4 is below 5%. (Solubility of MgSO_4 , 0.2 gm./100 ml. of alcohol).

To 25 ml. of 0.5N AgNO_3 solution in a clean 100 ml. beaker add exactly 1 gm. of sample. Stir the mixture with a Teflon coated magnetic stirrer for 5 minutes. Filter through a clean sintered glass Gooch crucible (fine). Wash the precipitate twice with 5 ml. (each) of 50/50 methanol-water mixture.

Dilute the filtrate to 100 ml. in a volumetric flask. The total amount of AgNO_3 is determined by titration with standard NH_4CNS using ferric alum as indicator.

Calculation

$$100 - (\% \text{H}_2\text{O} + \% \text{MgSO}_3 + \% \text{MgSO}_4 + \% \text{MgO}) = X$$

$$\% \text{MgO} + (\% \text{MgSO}_4 \times 2.05) = Y$$

$$\text{Amount of } \text{AgNO}_3 \text{ consumed per 1 gm. of sample} = C$$

$$\text{Corrected amount of } \text{AgNO}_3 \text{ consumed} = C + C \frac{(X + Y)}{100} = D$$

Determine the ratio of $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$: $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ from the graph.

Construction of graph

Draw a graph from the data in the following Table. Plot along X-axis the ratio of the two hydrates and the amount of AgNO_3 consumed on the Y-axis.

<u>Ratio of $3\text{H}_2\text{O}$</u> <u>$6\text{H}_2\text{O}$</u>	<u>gms. of AgNO_3 consumed</u>
100/0	2.1450
80/20	1.7960
60/40	1.4470
50/50	1.2725
40/60	1.0980
20/80	0.7490
0/100	0.4000

Note: The following elements interfere with this method:

Sulfide, all Halogens (except Fluoride), Cyanides,

Thiosulfate.

REACTIVITY TESTS

None of the procedures practiced in the Magnesia industry e.g. surface area measurements (by iodine method) or degree of hydration is applicable to this project. Hence, the following method was developed in order to measure the quality of regenerated MgO.

Magnesium oxide, in aqueous suspension, reacts with sulfur dioxide as:



Magnesium sulfite, being insoluble, precipitates out of the solution.

From the above equation:

40.31 gm. of MgO reacts with 64.06 gms. of SO₂.

Thus, the theoretical SO₂ removal capacity of MgO is

$$\frac{64.06}{40.31} \times \% = 100$$

The value of ' $\%$ ' being 62.93. In this procedure it is assumed that MgSO₃ is completely insoluble in water and no side reactions occur.

APPARATUS

Pure SO₂ gas-cylinder with single stage regulator (Model No. 71) from Matheson.

Flow meter (Roger Gilmore Industries, Inc.) No. 12 (Cat. No. F-2260A)

Two 3 - necked glass flasks (500 ml.)

Two gas purgers (sintered glass extra coarse porosity)

Magnetic stirrer (bar and plate)

500 ml. Volumetric flasks

Burettes (50 ml.)

Pipettes (5 ml. and 2 ml.)

REAGENTS

Caustic soda

Starch indicator

Standard iodine solution

Standard sodium thiosulfate solution

PROCEDURE

SO₂ gas flow is adjusted in such a manner that about 24 gms. of SO₂ pass through the purger in 20 minutes. The equipment arrangement for this test is shown in Fig. 1.

The amount of SO₂ passing through the system for any particular setting of the rotometer, is measured by absorption in 50% NaOH and subsequent titration of the sulfite by iodine solution.

From the amount of SO₂ passing through the system the theoretical amount of MgO necessary is calculated as follows:

Amount of SO_2 in grams $\times 0.6292$ = amount of MgO (in gm.) required.

The required amount of MgO , calculated as above, is placed in flask No. 1.

The 300 ml. of standard iodine solution, in the second flask, absorbs any SO_2 that escaped from flask No. 1.

After the passage of SO_2 through the system, the whole system is purged with air or nitrogen to remove any SO_2 in the line and transfer it into the two absorbers. The pH of the MgSO_3 - MgO slurry is measured.

The magnesium sulfite slurry is filtered under suction, washed twice with water. The filtrate is diluted to 500 ml. and the SO_2 content determined iodimetrically. The cake is washed with acetone, air and oven ($40^\circ\text{C}.$) dried and analyzed (if desired) for MgO , MgSO_4 , MgSO_3 and H_2O content. The contents of iodine flask is also diluted to 500 ml. and the SO_2 content is determined.

CALCULATIONS

Amount of SO_2 passed	'a' gm.
Amount of MgO taken (for 'a' gm. of SO_2)	'b' gm.
Amount of SO_2 in MgSO_3 filtrate	'c' gm.
Amount of SO_2 in iodine flask	'd' gm.

$$\text{SO}_2 \text{ removal capacity of MgO} = \frac{a - (c + d) \times 62.93}{b}$$

N.B. For routine purposes the iodine flask can be discarded, as only a small amount of SO₂ escapes from flask No. 1.

REMARKS

The SO₂ removal capacity is a pure and arbitrary number.

Because of the nature of assumptions made, e.g. insolubility of MgSO₃ in the slurry, no side reactions, disregarding bisulfite formation, etc., the results obtained are low. Thus, a value of 40 - 50 is considered to be good. Even virgin MgO, under these circumstances, gives a value of 60 - 65.